VOL. 1 No. 2
APRIL 1959

RNAL OF THE

LESS-COMMON METALS

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ROCKET PROPULSION

by

MARCEL BARRÈRE, *Head of the Research Division of the Office National d'Études et de Recherches Aéronautiques (ONERA), Paris (France)*

BAUDOUIN FRAEIJS DE VEUBEKE, *Professor at the Universities of Liège and Louvain (Belgium)*

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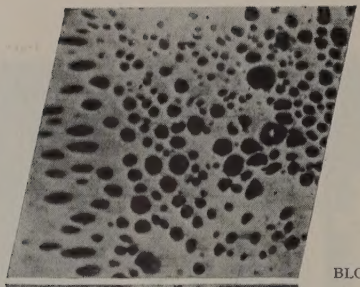

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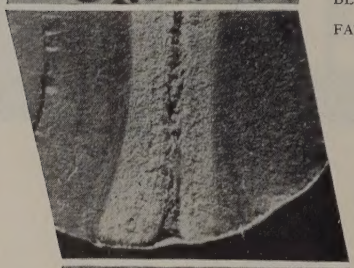

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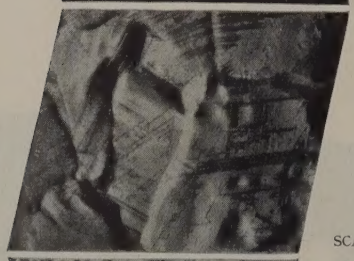

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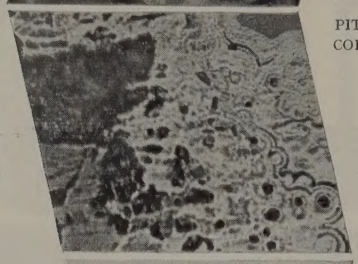

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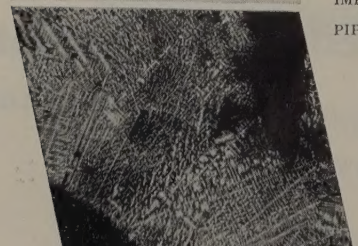

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their origin and elimination

by E. P. POLUSHKIN

Formerly Associate Professor of Metallurg Stevens Institute of Technology, Hoboken, N.J. (U.S.A.)

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THE STRUCTURE OF BERYLLIUM, WITH PARTICULAR REFERENCE TO TEMPERATURES ABOVE 1200°C

A. J. MARTIN AND A. MOORE

Atomic Weapons Research Establishment, Aldermaston, Berks. (Great Britain)

INTRODUCTION

Many references appear in the literature to an allotropic modification in beryllium, occurring within the temperature range 400–800°C, and several more relating to a double thermal arrest associated with the melting point. Early investigators, measuring electrical resistivity[1], specific heat[2], and lattice parameters[3,4], reported anomalous results with beryllium heated into the 400–800°C region, and attributed these to an allotropic modification. Recently, however, GORDON[5], using a high temperature X-ray technique, showed that the normal close-packed hexagonal structure remained stable between 20° and 1000°C, but this was disputed a year later by SIDHU AND HENRY[6]. Using X-ray techniques at 20°C and quenched beryllium–gold alloys they postulated the existence of a second phase, β, existing with α at room temperature. This β phase was complex hexagonal having 58 atoms/unit cell.

Similarly, the thermal analysis data of many workers[7–9] has shown that beryllium exhibits a double arrest at the melting point; one arrest being associated with the melting temperature at 1278–1284°C, and a lower arrest occurring at 1260–1263°C. Much controversy has centred on deciding whether this lower arrest is connected with the presence of a eutectic or with an allotropic modification. LOSANO[10], however, has reported finding only a single arrest using metal 99.96% pure.

With this background of information, research was begun at A.W.R.E., the purpose of which was to investigate these conflicting reports and to study the effect, if any, of purity on any solid-state changes observed. The study was conducted using electrical resistance measurements, thermal analysis and X-ray lattice parameter measurements; the first two over the temperature range 25°C to the melting point (1290°C) and the X-ray diffraction research from —196°C to the melting point. This report is concerned, in the main, with the evidence of the latter two studies, with particular reference to the results obtained above 1200°C.

THERMAL ANALYSIS APPARATUS

Conventional practice in differential thermal analysis was followed. The beryllium specimen, weighing about four grams, was placed in a beryllia crucible which rested on a nickel reference block in the centre of a tubular resistance furnace (see Fig. 1); other furnace details may be seen in Fig. 2, and consisted briefly of a tubular tantalum resistance element held at the top and bottom in restraining tungsten rings.

A pyrophillite tube, supported inside the furnace element served to protect the differential assembly from small but rapid temperature variations due, for example,

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to sudden changes in furnace voltage, and also served to cut down convection currents in the argon atmosphere.

Heating or cooling rates of 1° to 5°C per minute were readily maintained between room temperature and 1300°C.

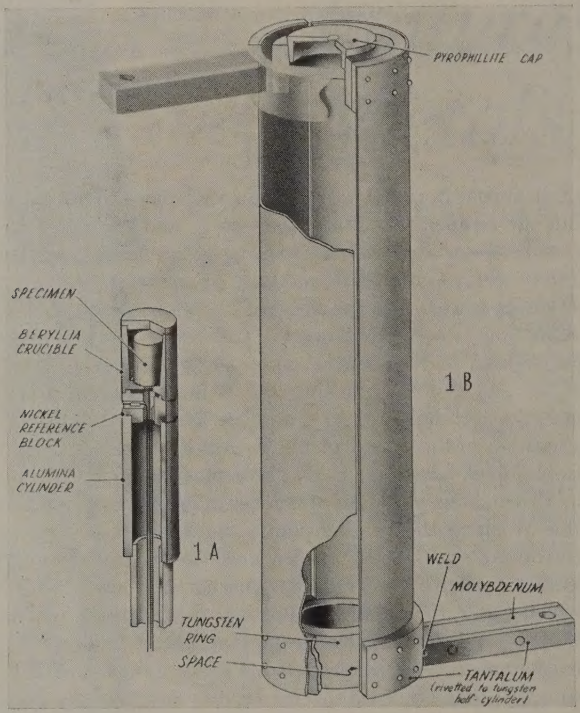

Fig. 1a. Crucible and reference block.
Fig. 1b. Current lead in assembly (without inner furnace tube).

Measurement of temperature differential

Three platinum–13% rhodium/platinum thermocouples were attached to the crucible and reference block assembly. Two of the couples — one in the crucible and one in the reference block — were connected in series opposition to a d.c. amplifier. The amplified signal was then fed to three points of a four point, rapid response, 0–1 mV recorder and the position of the trace on the chart could be varied by opposing the output voltage with an external and continuously variable e.m.f.

The potential from the third thermocouple (with its junction in the reference block) was also opposed by a separate potential divider circuit, which could be varied in 1 mV steps. The resultant e.m.f. was fed to the fourth point on the recorder so that the two traces — the amplified differential signal and the temperature —

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appeared on the same chart. When the temperature trace reached the maximum on the chart the back e.m.f. was increased by 1 mV to return the trace to the zero position.

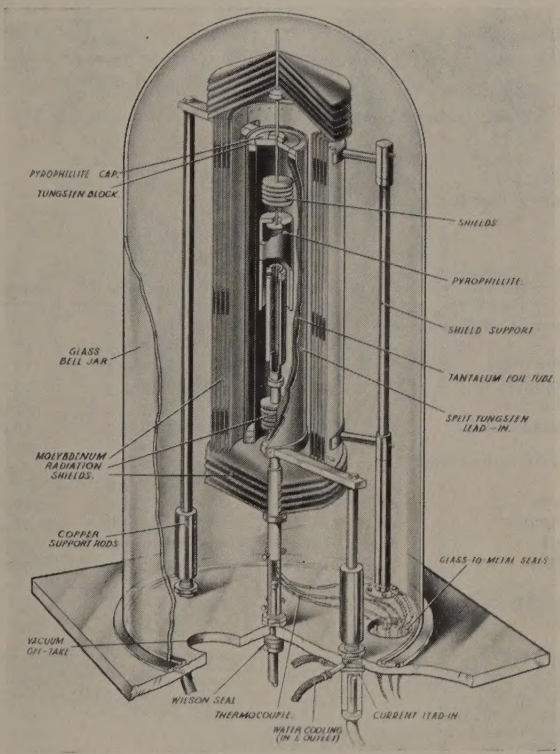

Fig. 2. Thermal analysis furnace.

EXPERIMENTAL RESULTS

Heating and cooling curves were produced for beryllium specimens of varying impurity content, including commercial purity metal, the pure and impure portions of a zone refined bar, and the condensate and residue from a vacuum distillation process. The results of spectrographic analyses of these samples are given in Table I.

No evidence of a solid-state change between 25° and 1200°C was detected in any experiment. A study of the traces above 1200°C, however, revealed the double thermal arrest in the region of the melting point which has been described by other workers[7–10]. In all cases, in addition to the melting point arrest, which started at temperatures between 1286.9° and 1291.9°C and between 1291.9° and 1280.4°C on cooling, depending on the sample, a second arrest was found which started at an average of 17°C below the first on heating and 20°C below on cooling. A full summary of the results is shown in Table II.

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TABLE I

Element	Zone refined			Distillation	
	Stock	Purified	Impure	Distillate	Residue
Al %	0.04	0.006	0.110	0.022	0.022
Fe %	0.08	0.012	0.10	0.026	0.048
Si %	0.066	0.026	0.068	0.037	0.044
Mn %	0.004	0.002	0.005	0.0008	0.002
Cr %	0.002	0.003	0.004	0.0003	0.001
Ni %	0.007	0.005	0.006	N.D.	N.D.
Mg %	0.002	0.002	0.002	0.003	0.004
H_2 c.c./g	0.4*	0.4*	0.4	0.42	N.D.
O_2 %	0.012*	0.008*	0.016	0.140	N.D.

* Analysis made on similar bar.

TABLE II

Material	Temp. 1st arrest °C	Temp. 2nd arrest °C	Difference
Arrest points on heating			
Ingot	1268.5	1287.2 ±3	18.7
Z.R. pure	1271.1	1289.8 ±3	13.7
Z.R. impure	1274.7	1291.9 ±3	17.2
Distillate	1271.9	1289.3 ±3	17.4
Distillation residue	1268.9	1286.9 ±3	18.0
Arrest points on cooling			
Ingot	1282.2	1254.7 ±3	27.5
Z.R. pure	1291.9*	1272.7 ±3	19.2
Z.R. impure	1284.8	1263.4 ±3	21.4
Distillate	1284.6	1263.9 ±3	20.7
Distillation residue	1280.4	1259.4 ±3	21.0

* Results considered to be low by 4–5°C.

Fig. 3. Portion of typical heating curve showing two arrest points ~ 1250–1280°C.

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In all but two cases the figures shown represent the average of at least two separate thermal analysis experiments conducted with the specimens concerned. A typical heating and cooling curve is given in Fig. 3 which is, in fact, the observed heating curve for zone refined metal: the temperature trace is the dotted line running diagonally across the chart from left to right.

The most significant feature of these results appears to be the similarity in shape of the curves obtained on heating and cooling. This cannot be interpreted on the basis of a eutectic or peritectic reaction. Consider for example a binary eutectic diagram as in Fig. 4A and an alloy composition represented by the vertical broken

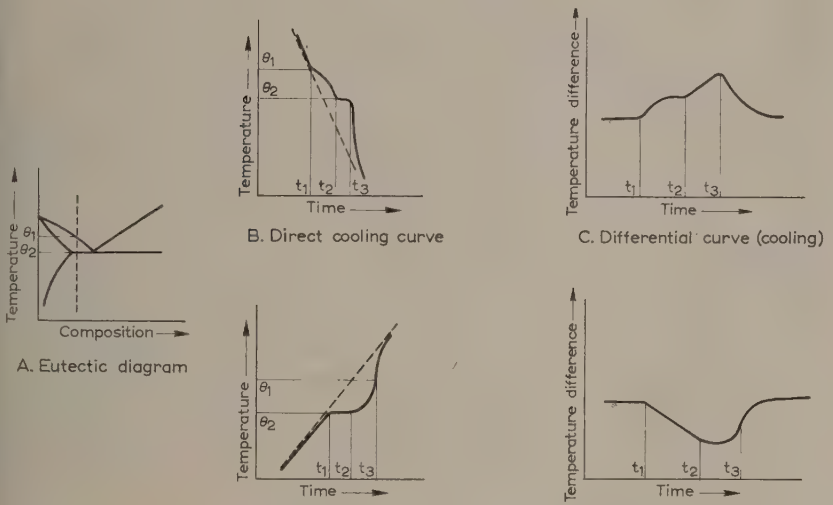

Fig. 4. Eutectic system.

line. The type of direct cooling curve that would be expected is shown in Fig. 4B. In this, the broken line represents the cooling rate of the furnace or of a reference block. A differential cooling curve, resulting from the difference in the temperature of the reference block and the alloy specimen should then appear as in Fig. 4C. Under these circumstances a distinct double arrest on cooling could result. Considering the type of curves likely to be obtained on heating, however, it would appear to be most unlikely that a distinct double arrest would be found, see Figs. 4D and E. Following the same line of argument, a peritectic reaction would appear to be equally unlikely. By contrast, however, a double arrest is expected in pure metals and dilute alloys undergoing an allotropic transition on heating and cooling, see Fig. 5. Moreover, in considering the results actually obtained with the beryllium samples two other factors appeared to militate against the existence of a eutectic or peritectic. These were that, although the impurity content varied considerably from one sample to another,

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(a) the temperature difference between upper and lower arrests was approximately the same in all cooling runs and all heating runs, and

(b) the relative magnitudes of the two arrests also appeared to be a constant value.

It would appear, therefore, that the anomalous arrest below the melting point was probably due to an allotropic transition. Positive evidence of this, however, could only be obtained by an X-ray study conducted up to the melting temperature of 1290°C and work was subsequently continued along these lines.

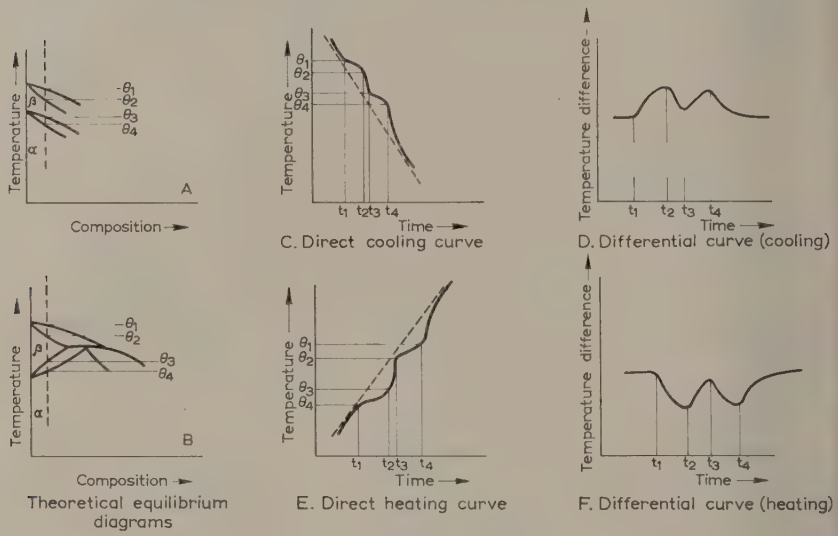

Fig. 5. Proposed systems.

X-RAY DIFFRACTION STUDY

Experimental conditions

The lattice spacings of beryllium, 99.4 wt.-% pure and containing 0.3 wt.-% BeO, 0.1 wt.-% Al, 0.1 wt.-% Fe and measurable quantities of B, Si, Na, Ca, Mn, Co, Ni and Cu have been measured at temperatures within the range -193° to 1265°C. The experiments have been carried out in the Unicam High Temperature X-ray Camera using fibre specimens. It has been necessary, however, to modify the camera in order to obtain optimum working conditions for:

(i) control and uniformity of specimen temperature to better than $\pm 2°$ at temperatures $<1000°$ and better than ± 3°C at temperatures >1000°C.

(ii) vacuum 5×10^{-5} mm Hg at 1250°C.

(iii) contamination of the specimen by platinum which volatilises from the naked furnace windings >1150°C.

The use of conventional powder specimens sealed in silica quills has only been possible below 700°C: above this temperature suitable solid and fine grained (40 μ) fibres have been mechanically and chemically machined from sintered rods of berylli-

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um. Fortunately, grain growth has not occurred in these sintered fibres until 1220°C and even this has not been an embarrassment; in fact the "spottiness" of the beryllium diffraction spectrum makes it readily distinguishable from the beryllium oxide and any other contaminate spectra.

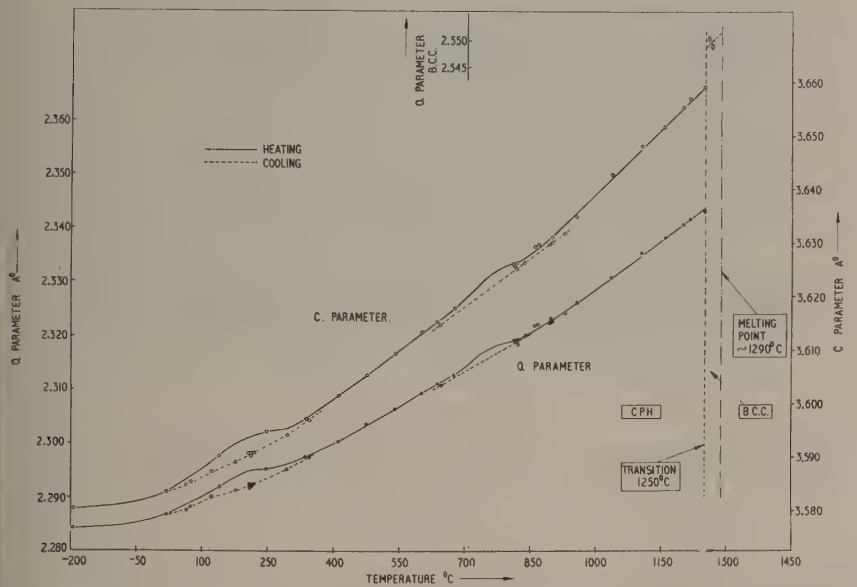

Fig. 6. The effect of temperature on the lattice spacings of beryllium: the anomalous behaviour at 200 and 800°C is not associated with the allotropic transition but is believed to be due to the solvent properties of beryllium.

Experimental observations

Fig. 6 shows the effect of temperature on the lattice spacings of beryllium: the full line is the trace obtained on heating and the dotted line the subsequent cooling trace from 960°C. The deviations from linearity at ~200° and ~800°C may be attributable to the effect of solutes. It is only at ~1250° that a discontinuity is found and coincides with the complete transformation of the closer-packed-hexagonal structure (α) to that of a body-centred-cubic (β). The transformation is reversed by cooling to 1244°C and thus shows ~5° hysteresis.

Fig. 7 shows the relevant diffraction spectra near the transition temperature: the b.c.c. spectra are visible below line 10.

Discussion

The closest distances of approach of the atoms in the two structures at 1250°C are 2.276 Å and 2.208 Å for the c.p.h. and b.c.c. structures respectively. This difference of 3% is expected to result from the change in co-ordination number of 12 to 8 for

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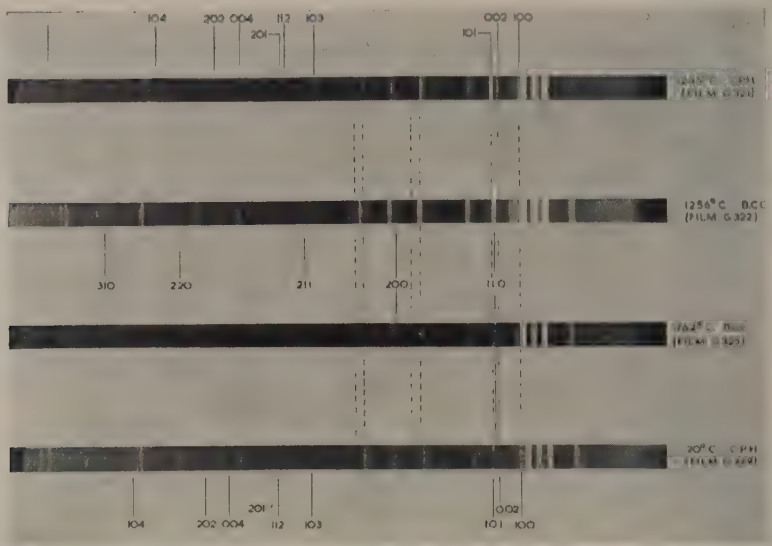

Fig. 7. High temperature X-ray diffraction spectra of beryllium showing the alternative structures c.p.h. below 1250°C; b.c.c. above 1250°C. The beryllium spectra in each case are indexed and readily distinguished from the oxide and other contaminant spectrum by the inherent "spottiness" due to grain growth of the metal. The three split and diffuse lines which are adjacent to the 100 c.p.h. beryllium line are due to oxide and the splitting is associated with the large effective diameter of the heavily oxidised beryllium wire specimen.

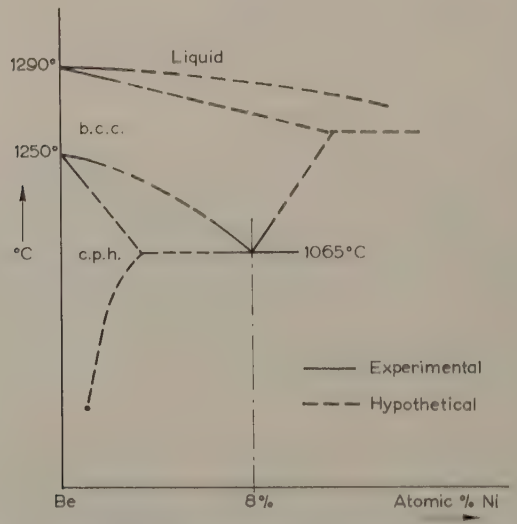

Fig. 8. A possible phase diagram for the beryllium–nickel system.

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the two structures[11]. It is unlikely, therefore, that β beryllium has any greater solvent properties for the inherent impurities than α. By contrast, however, it is possible that the α/β transition is not observed in pure beryllium as implied in LOSANO's observation.

It is yet too early, however, to say whether the α/β transition can be exploited to affect, and hopefully to improve, the mechanical properties at low temperatures. The cast metal normally shows a coarse columnar structure with no evidence of any grain refinement or precipitation characteristic which could be attributable to the α/β transition: indeed single crystals are readily grown from the melt by zone refining methods. S. H. GELLES *et al.* (Nuclear Metals Incorporated, Jan. 1958) have recently reported X-ray absorptiometric measurements on diffusion couples which have implied that a eutectoidal change is centred at 8 wt.-% nickel and 1065°C. It is reasonable to hope that this change is related to the α/β transition (see Fig. 8), and work is proceeding at A.W.R.E. to examine this possibility. If the β/α transition can be made to occur at temperatures $\sim$1000°C it may be that grain refinement and associated improvement in mechanical properties can be obtained.

It is thought unlikely, however, that the β/α transition can otherwise affect the structure or properties either at room temperature or at reactor temperatures ($<$600°C) without the addition of large and prohibitive alloying elements.

ACKNOWLEDGEMENTS

The work has formed part of a general research and development programme on beryllium led by MR. G. C. ELLIS whom we would like to thank for his encouragement.

In particular we would like to acknowledge the active interest and experimental work carried out by MR. K. L. EDWARDS (thermal analysis) and MR. D. A. CHEER (X-ray diffraction).

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SOME INTERESTING PROPERTIES OF PYROLYTIC CARBON*

Royal Aircraft Establishment, Farnborough, Hants. (Great Britain)

INTRODUCTION

Although carbon and graphite are not really metallic substances, it is felt that their unique high temperature properties are of great interest as indicating a possible material for applications at temperatures above 2000°C when the application of metallic substances becomes very difficult. The paper does not attempt to give an exhaustive account of any particular research work, but describes a number of interesting results which have been obtained during general studies of carbon and graphite.

I. THE STRUCTURE AND DENSITY OF PYROLYTIC CARBON

A. R. G. BROWN, D. CLARK AND J. EASTABROOK

Production of pyrolytic carbon

The production of pyrolytic carbon has already been described[1]. It is produced by the pyrolysis of a hydrocarbon vapour, with or without diluent gases, on to a graphite filament maintained at the desired temperature by the passage of a low voltage high amperage current. The pyrolysis may be carried out at pressures between 5 cm and 70 cm Hg pressure, and the hydrocarbon used does not seem to affect significantly the nature or properties of the deposit obtained at a given temperature. Benzene, methane, propane and carbon vapour have been used as sources of carbon and only minor differences have been found in the structure of deposits produced at a given temperature. All of the material referred to in this paper has been produced from propane at 15–20 cm Hg pressure.

Optical examination in polarised light

Fig. 1 shows the structure of a series of deposits produced at different temperatures. The photomicrographs are all of cross-sections of the deposit (which have been polished using normal metallographic techniques), taken with partly crossed nicols. Fig. 1a shows a deposit produced at 2100°C and the fine, regular fan-like structure is most marked. The dark horizontal lines represent circumferential cracks in the material probably caused by differential thermal expansion effects. Fig. 1b shows a deposit produced at 1900°C, and the difference in structure is striking. The fine

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structure has largely disappeared, and a more "block-like" structure of conical elements is seen.

In Figs. 1c, d and e structures of deposits produced at 1700°, 1600° and 1400°C are shown, and here the block-like structure is very marked. It is of interest to note that the structures of all these deposits are very similar, and in fact it is almost impossible to distinguish between deposits produced at temperatures between 1400° and 1800°C.

Fig. 1a. Deposit produced at 2100°C.

Fig. 1b. Deposit produced at 1900°C.

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Optical examination of etched specimens

A recently developed method[2,3] enables carbons and graphites to be etched by bombardment with argon ions. The specimen is made the cathode in an apparatus consisting of anode and cathode with appropriate screens under an evacuated bell jar. Approximately 2 kV are applied across the electrodes, and etching carried out with a current of about 10 mA at an argon pressure of 50–75 μ.

Etching by this technique makes it possible to remove the surface layers of polish-

Fig. 1c. Deposit produced at 1700°C.

Fig. 1d. Deposit produced at 1600°C.

References p. 100

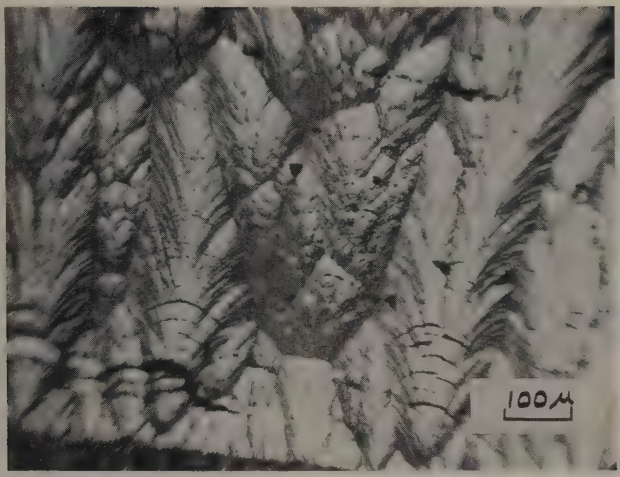

Fig. 1e. Deposit produced at 1400°C.

ng debris and obtain photomicrographs in normal incident light. Fig. 2 shows such photomicrographs of deposits produced at 2100, 1900 and 1400°C. The high temperature (2100°C) deposit again shows a very fine structure. However, it should be noted hat the apparent orientation of the structure is different from that seen under olarised light, the fine lines now being parallel to the substrate. These fine markinge re thought to arise from the removal of carbon atoms from the edges of the c-planes f the carbon. Fig. 2b shows that the 1900°C deposit still retains some traces of thess narkings, but in addition has marked "grain boundary" type structures correspondng to the blocks seen under polarised light. The low temperature deposit (Fig.2c) hows no sign of the high temperature structure but shows the development of a fine an-like structure within the main "blocks".

Electron micrographs

The development of this etching technique has enabled replicas suitable for xamination on the electron microscope to be produced. Electron micrographs of leposits produced at 2100°, 1900° and 1700°C are shown in Figs. 3a, b and c. These tructures have not been interpreted in any detail. However, the fine structure shown in ig. 2a corresponds with that of Fig. 3a and Fig. 3b shows a "grain boundary" of the type een in Fig. 2b. Fig. 3c is of interest in that it shows no signs of any major porosity.

Variation of density with deposition temperature

It was discovered early in our work[4] that the density of deposited carbon varies n a most striking manner with the temperature of deposition. The variation has now een followed to much lower temperatures than originally reported (Fig. 4).

At high temperatures (2100°C and above) the density approaches the X-ray density f true graphite (2.26 g/cm³) but as the temperature of deposition is lowered it falls

References p. 100

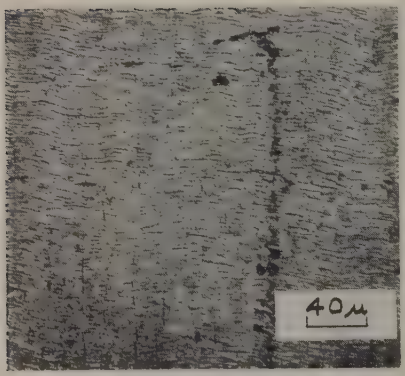

Fig. 2a. Deposit produced at 2100°C.

Fig. 2b. Deposit produced at 1900°C.

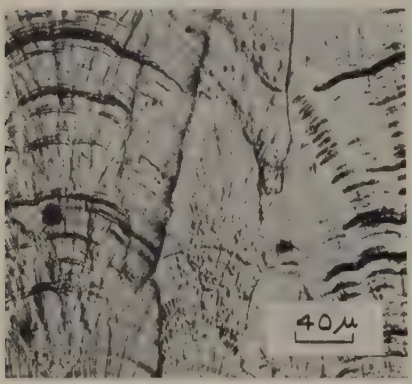

Fig. 2c. Deposit produced at 1400°C.

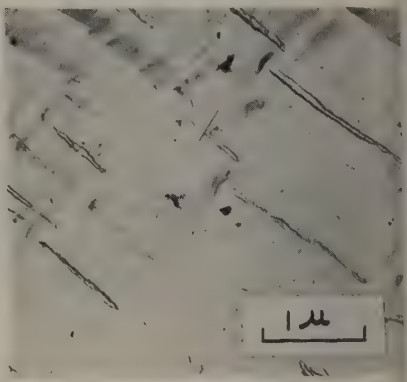

Fig. 3a. Electron micrograph of deposit produced at 2100°C.

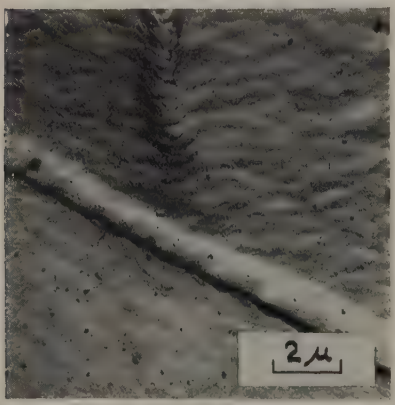

Fig. 3b. Electron micrograph of deposit produced at 1900°C.

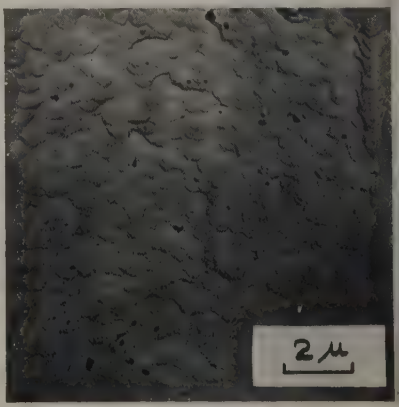

Fig. 3c. Electron micrograph of deposit produced at 1700°C.

rapidly. At about 1750°C the density reaches a minimum of about 1.2 g/cm³, roughly half that of the high temperature deposits. As the deposition temperature is further lowered the density of the deposit again increases, and though never reaching the value for the high temperature deposits (max. 2.24 g/cm³) does rise to the remarkably

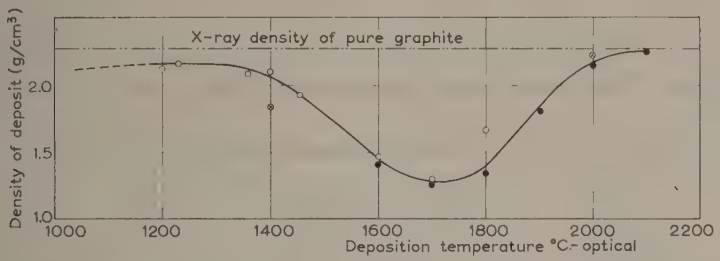

Fig. 4. Variation of density of deposited carbon with temperature of deposition.
● previous work.
○ present work; deposited from propane.
⊗ present work; deposited from methane.

high value of 2.1 g/cm³ at 1350°C, and remains above 2.0 g/cm³ to the lowest deposition temperatures yet investigated. Although the density of the deposits formed at about 1750°C is so low, there is no evidence of macro porosity in these materials (see Fig. 3c) and the cause of the low density is uncertain.

X-ray examination

X-ray examination reveals further interesting features. The deposited carbon is, in general, turbostratic, *i.e.* consists of layers of hexagonal arrays of carbon atoms parallel to each other, but otherwise randomly oriented, and is laid down with these layers (c planes) parallel to the surface of the substrate. In the present work interest has been centred on the X-ray powder photographs. These were taken in a 19 cm camera using monochromatic CuKα X-rays, and exposures of about 24 hours. At first sight the photograms form a series in which the disordering of the deposit continuously increases. This is shown by increasing width of the 002 line and disappearance of higher angle reflections. However, measurement of the band widths show that the series is not continuous. This is illustrated in Figs. 5 and 6 in which the widths at half height for the 002 line and 10 bands are plotted against deposition temperature. It would appear that a sharp peak is superimposed on a general curve of increasing width with decreasing temperature of deposition. This peak occurs in the temperature range at which minimum density is found. Further the deposits made at 1600° and 700°C show evidence of low angle scattering, though this has not been analysed.

The interpretation of these results is difficult as either one of two possible processes could lead to the observed effects. The possible explanations for the peak in band width are

(a) a marked drop in the size of the layer planes,

(b) development of fine porosity with increased separation of the layer planes.

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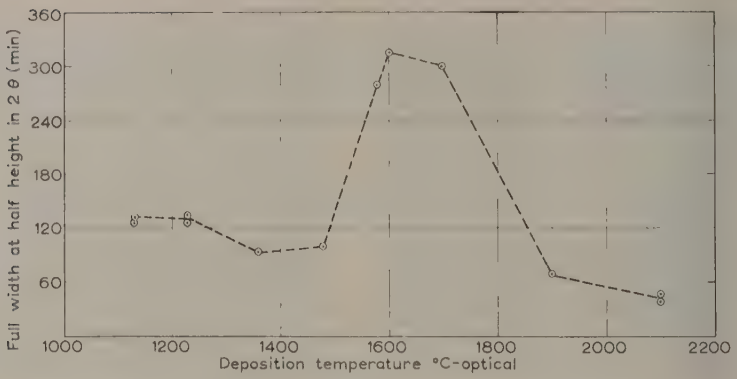

Fig. 5. Variation in width of 002 reflection with temperature of deposition.

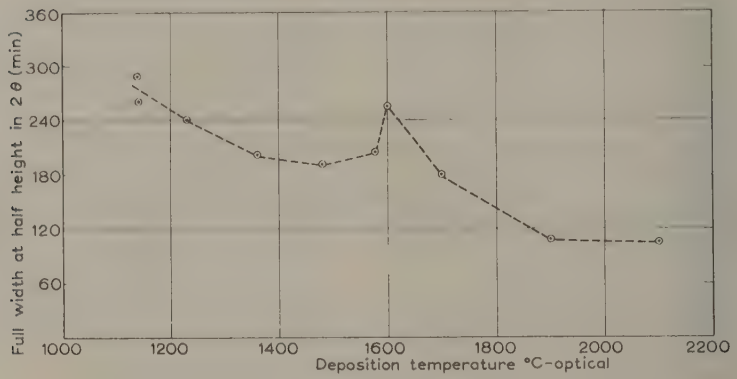

Fig. 6. Variation in width of 10 band with temperature of deposition.

Either of these explanations would also account for the low angle scattering, and further work would be necessary to decide which is responsible for the present phenomena.

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II. DEFORMATION OF DEPOSITED CARBON

F. J. BRADSHAW AND C. WHEELER

We have carried out some experiments on the way in which the graphites laid down at high temperatures (2100° - 2200°C) deform when under three-point loading; the load was applied parallel to the c-axis.

At room temperatures, failure is by lamination with the laminae breaking up into fragments. There is no visible slip along the basal planes before this occurs. At high temperatures (2000°C) the same thing happens, but an additional mode of deformation also occurs, resulting in "flecks" appearing across a section. Fig. 7a shows the original structure of the material deposited at high temperature and Fig. 7b the deformed material in which a number of bright flecks can be seen. All the photographs have been taken in polarised light to show the deformed structure. The flecks normally lie at about 45° to the local c-direction and are obviously caused by the graphite layers kinking. Since the local maximum shear direction is also at 45° to the c-direction it might be thought that the fleck direction is related to it. However in Fig. 8 the fleck angle can be seen to alter in the fan-like region of different orientation although the load is the same everywhere, so the local c-direction is obviously important.

Deformation twins have been observed in graphite single crystals[1] and the flecks are very like twins. However they cannot be true twins since the material is turbostratic, so that a co-ordinated twin displacement of planes would seem to be impossible; also although the angles between the twinned and original planes are ap-

Fig. 7a. Original deposited carbon.

Reference p. 105

Fig. 7b. Deformed material.

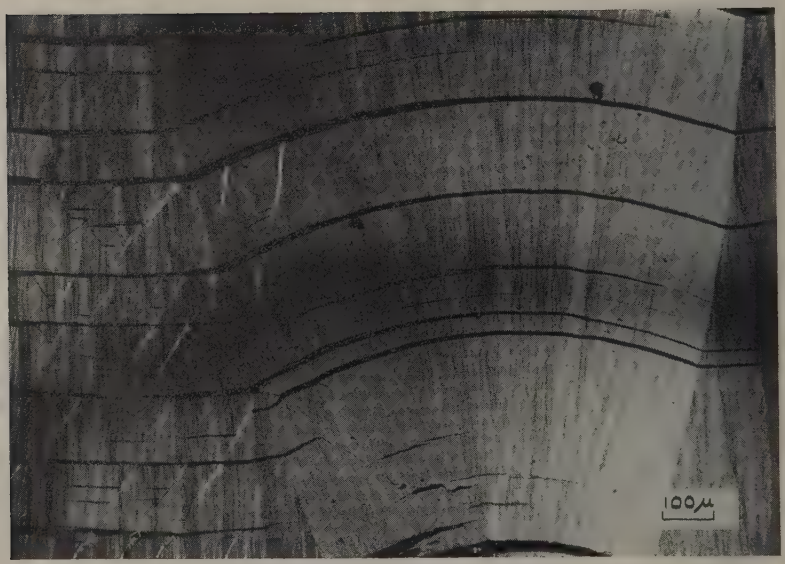

Fig. 8. Flecks in material showing orientation changes.

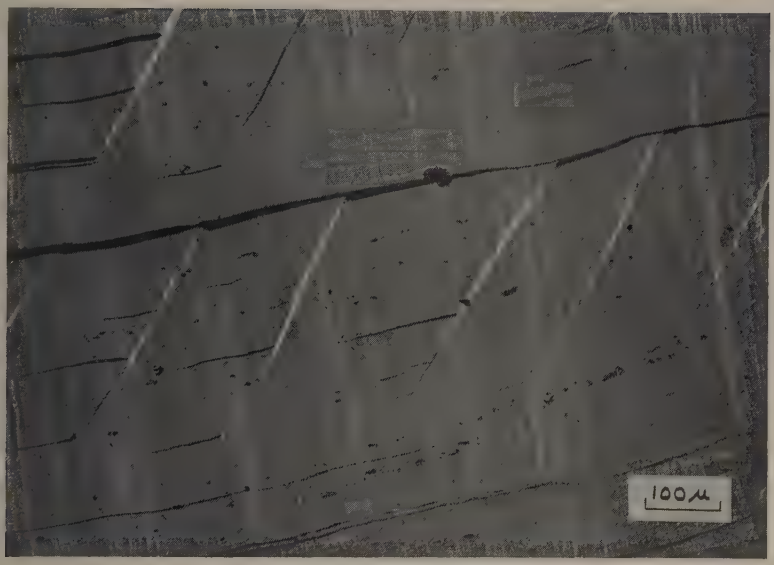

Fig. 9a. Flecks visible after first loading

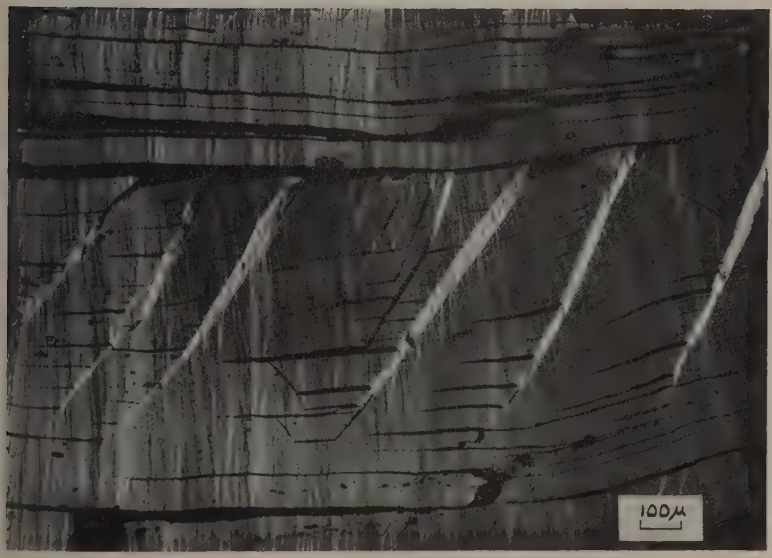

Fig. 9b. Flecks increased in number and size after second loading.

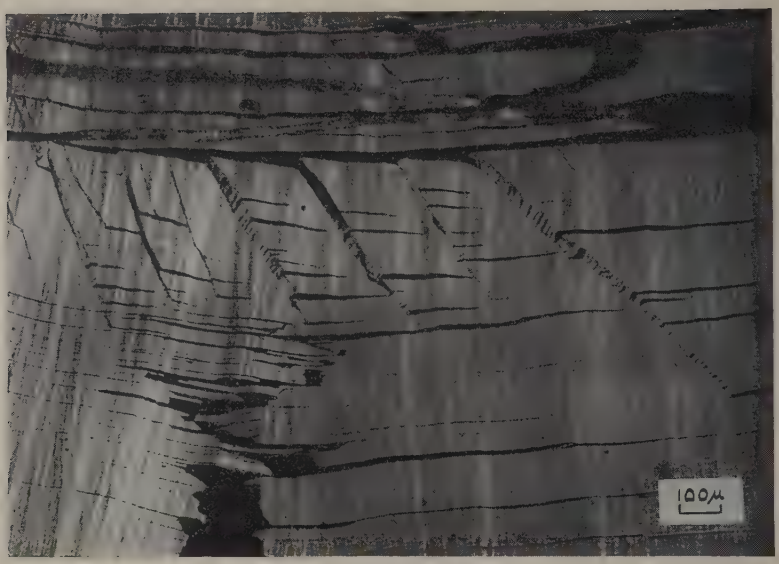

Fig. 10a. Deformation flecks.

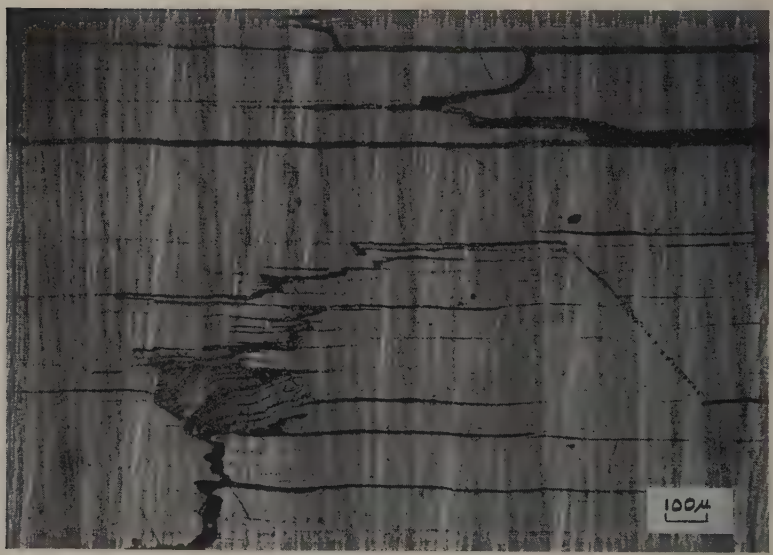

Fig. 10b. Deformation flecks after reversal of load.

proximately those one would predict from the geometry of the graphite lattice they have a spread about a mean value. The flecks are best described as deformation twins degraded by the imperfections in the basic graphite structure.

If the loading is increased or repeated the flecks increase in number and size as shown in Fig. 9. Fig. 9a shows the flecks visible after one loading and Fig. 9b the same field after loading for a second time. In Fig. 10 the effect of reversing the load is illustrated. Fig. 10a shows the usual deformation flecks, Fig. 10b shows the same field after the reverse load had been applied. The smaller flecks have been eliminated and even the larger flecks have recovered to the extent of leaving only fine scars. One would not expect the material in the large flecks to have recovered completely, but re-loading the specimen again in the original direction showed that whereas the large flecks reappeared, new patterns of small flecks were created. From this we conclude that, on a small scale, this form of deformation may be truly recoverable.

It is interesting to see that the same sort of deformation can be produced in natural graphite. Fig. 11 shows a section of natural graphite in which the flecks have been produced by mechanical loading at 2000°C.

There does not appear to be very much difference, from X-ray data, between the microstructures of our graphites deposited at 2100°–2200°C and that of the usual manufactured artificial graphite heated to the same temperature except that the regions of similar orientation in the latter are very much smaller. Accordingly we suggest that a mode of deformation similar to that described above may well occur on a smaller scale in such commercial graphites.

Fig. 11. Flecks produced in natural graphite.

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FURNACES FOR THE STUDY OF HIGH TEMPERATURE EQUILIBRIA

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INTRODUCTION

Laboratory furnaces for the heat-treatment of metallurgical specimens at temperatures above 1200°C can be divided into four kinds, this division having a close relation to the temperature range for which a given type of furnace is suitable.

I. CONVENTIONAL WOUND FURNACES

1200–1550°C. Platinum wound alumina tube furnaces are in widespread use and are conventional equipment in most metallurgical laboratories. They provide a relatively robust piece of laboratory equipment, and can be used at temperatures up to 1600°C if the corresponding reduction in life is acceptable.

1500–1800°C. Molybdenum wire or tape wound on an alumina tube, and run in hydrogen or cracked ammonia has found wide application in industrial use. Such furnaces are very suitable for virtually continuous operation at temperatures up to 1750°C, and there is at least one commercially available molybdenum wound furnace of a size suitable for laboratory work.

Such furnaces do not provide a large advance over the range covered by a platinum (or platinum–rhodium alloy) furnace. Attempts to extend the range of these furnaces based on a conventional design (using alternative refractories such as thoria for the support of a molybdenum or tungsten winding) are in general not very successful — presumably due to difficulty with the refractories and the associated requirement of keeping a winding with a relatively small cross-section at high temperatures for long periods.

II. INDUCTION HEATING

1200–2000°C. In principle this technique should only be limited by the refractory used, although in practice the necessity for non-metallic refractory radiation screens leads to difficult outgassing problems with certain metals. In addition, when working on a small scale the coupling between the work coil of the oscillator and the specimen is not very efficient. Whilst this method is very suitable for preparing alloys (eddy currents causing turbulence in the melt) it has largely been superseded in this respect by the argon arc furnace. Close control over the temperature is not very easy, and this has not favoured its application to the heat-treatment of alloys.

III. HIGH CURRENT FURNACES

This type of furnace has the advantage that refractories can, if necessary, be ex-

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cluded from the hot zone, and the heating element is fairly robust having a relatively arge cross-section. In addition the temperature can be closely controlled.

Carbon or graphite tubular heaters have been used to temperatures above 2500°C, ınd are very robust. Both the Tammann type of carbon tube furnace, which was devel-)ped in Germany, and the stacked carbon ring furnace of ROSENHAIN AND COAD-PRYOR[1] would appear to be suitable for some metallurgical problems although, above 2000°C, the presence of carbon vapour restricts its application.

Refractory metal heaters have been used at temperatures up to 2700°C and are suitable 'or most metallurgical work on the refractory metal alloys. The metals commonly ısed are tungsten, tantalum or molybdenum and these must be used in vacuo or an nert atmosphere.

Spiral tungsten elements have been used by ALBERMAN[2] and SCHOFIELD[3] at tempera-ures up to 2500°C. The cross-section of the tungsten rod used in making the spirals ıas to be sufficient to prevent appreciable creep occurring at the higher temperatures. SOWMAN AND ANDREWS[4] have also used a furnace with such an element. A larger

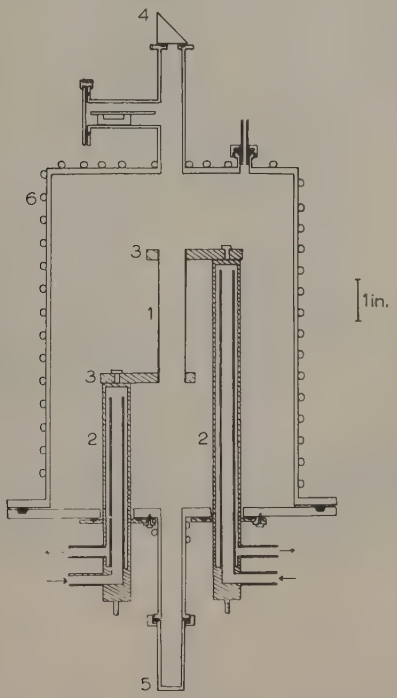

Fig. 1. Mk. I.

1) The tungsten tube heater, with both cylindrical and end radiation screens omitted.
2) Water cooled copper electrodes.
3) Copper electrodes.
4) Prism, for use with the optical pyrometer.
5) Quenching vessel.
6) Evacuated, water cooled, outer furnace case.

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furnace with a fabricated tubular tungsten heater has been described by RENDALL[5] and has been used up to 2400°C. The replacement of an element is not easy, however, and there is every advantage in having a small hot zone with heater of simple design, if possible.

A furnace with a tubular tantalum heater has been described by ORIANI AND JONES[6] who used it to measure the solidus points of alloys up to 2200°C. A small furnace with a split tungsten heater has been used by BICKERDIKE[7] at temperatures up to 2500°C.

Full details of the two furnaces which are the subject of this paper have been published elsewhere[8].

Their essential feature is the simple, inexpensive, fairly rugged, easily replaced heater tube which is made from 0.004 inch thick tungsten sheet. The first one, Mk. I, was built in 1955 and has been in operation at temperatures up to 2300°C since then. The tungsten tube was about 3 inches long and was held between water cooled copper electrodes, shown in Fig. 1. The expectation of life of the heater elements was found to be rather erratic, but approximately fifty heats at temperatures up to 2000°C reducing to about twenty at 2300°C were obtained. Mk.II was made with more efficient water cooling of the electrodes, as shown in Fig. 2, and has proved satisfactory at temperatures up to 2700°C. However, the life of the tungsten heaters is rather short at these high temperatures, averaging about six heats at 2600°C, although the relatively simple task of replacing a heater does not make this a serious difficulty. The control

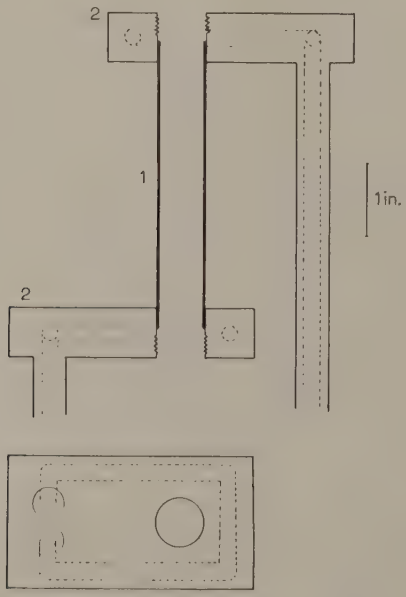

Fig. 2. Mk. II, modified electrodes, side view and plan.
(1) Tungsten heater tube with both concentric and end radiation screens omitted.
(2) Water cooled copper electrodes.

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over the temperature obtaining in the furnace is in the neighbourhood of ± 10°C at temperatures above 2000°C — an error only just greater than the sensitivity of the optical pyrometer used to measure temperature.

IV. THE ARGON ARC FURNACE

For temperatures above 2700°C this is the only type of furnace which is in widespread use in metallurgical laboratories. Whilst well suited to the preparation of many refractory metal alloys under very pure conditions, the maintenance of steady conditions and the uncertainty of emissivity corrections lead to difficulties.

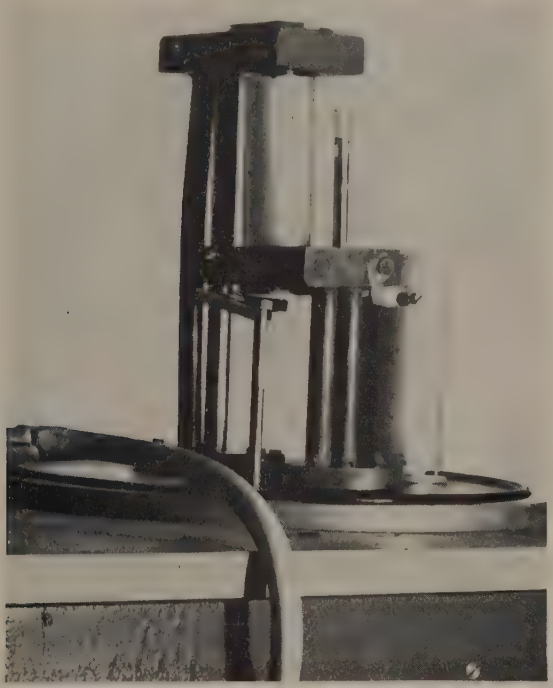

Fig. 3. Mk. II, showing the electrodes with heater element and radiation screens in position. A crucible and supporting stand are seen standing to the right of the heater element.

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SOLID STATE TRANSITIONS IN MANGANESE AND IRON SOLID SOLUTIONS

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The form of the equilibrium diagrams for binary alloys of metals in the B sub-groups of the periodic table can be related to electron : atom ratios, regarding the component metals as exhibiting their "group valency". This relation, together with the consideration of relative atomic radii, enables one to understand the general form of the alloy diagrams and has received considerable theoretical justification.

In the alloys of the transition metals, while the effects of atomic size are still evident, there does not appear to be any satisfactory explanation in terms of electron : atom ratios. However, the forms of the binary diagrams can be related to the structures of the component metals themselves. In particular, the transition from face centred cubic to body centred cubic structure which is exhibited in the first three transition series has been the subject of recent theoretical dicussion[1]. The importance of this f.c.c. - b.c.c. transition has also been recently demonstrated by HAWORTH AND HUME-ROTHERY[2], the sequence of structures of intermetallic phases being related to the metals concerned.

At elevated temperatures many of the transition metals show allotropic modifications, and in particular in manganese and iron there occur the γ (f.c.c.) and δ (b.c.c.) allotropes in the same sequence with ascending temperature:

$$\gamma \text{ Mn} \text{ — } 1135^\circ \text{ — } \delta \text{ Mn} \text{ — } 1245^\circ \text{ — Liquid}$$

$$\gamma \text{ Fe} \text{ — } 1390^\circ \text{ — } \delta \text{ Fe} \text{ — } 1535^\circ \text{ — Liquid}$$

In these temperature ranges, manganese and iron base alloys show the same structural changes, and moreover by examining binary alloys with other transition metals, it is possible to measure the extent to which any solute element favours either structure (f.c.c. or b.c.c.) when dissolved in manganese or iron.

The relevant portions of the phase diagrams have already been determined in detail for both manganese and iron base alloys with the first transition series, and for iron with the second transition series[3, 4]. Further work[5] on manganese base alloys completes the two series of diagrams with both transition series.

At the temperatures concerned (~1000°C for manganese and >1300°C for iron) the phase transitions in these alloys may be accurately detected by thermal analysis. The type of apparatus used has been described fully elsewhere[3, 6] together with the methods used for the various alloys. It is based upon a platinum resistance furnace through which passes a vacuum tight refractory tube which is either continuously evacuated or contains an inert gas. The most important feature of the apparatus is

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that specimens may be moved up and down within the vacuum tube without breaking the seal, this saves time in operation and also increases the life of furnace windings.

Interpretation of thermal arrests was straightforward with the exception of the melting point and solidus arrests in "pure" manganese and manganese base alloys. There appeared to be a second arrest some 3–4°C below the melting point and this has been described elsewhere[3].

Concentrating only upon the f.c.c.–b.c.c. transition temperature, and its elevation or depression by solute elements, it is possible to classify elements as b.c.c. or f.c.c. favouring. It is apparent from the results that this tendency to favour one or the other structure is the same for a given solute in manganese or iron. As might be expected

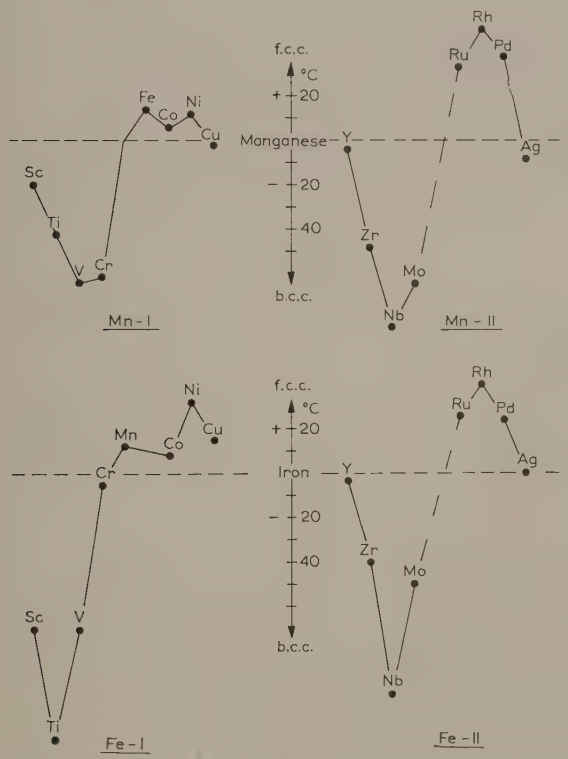

Fig. 1. Change in γ:δ transition temperature for 1 at.-% solute.

the solute elements favour that structure which they have themselves. It is also possible to go a little further and to use the slopes of the f.c.c.–b.c.c. phase boundaries as a measure of this tendency.

The results for the four series, manganese and iron with each transition series, can be represented as in Fig. 1. The elevation (f.c.c. tendency) or depression (b.c.c. ten-

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dency) of the $\gamma : \delta$ transition temperature is measured for 1 at.-% solute and the values plotted against the atomic number of the solute elements. The resultant plots show the maximum b.c.c. tendency in groups IV, V and VI, and the maximum f.c.c. tendency at the end of the series. The agreement between the sequence for the first transition series in each solvent is only approximate, but that for the second transition series is very close.

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METHODS FOR DETERMINING THE THERMODYNAMIC ACTIVITIES OF ALLOY CONSTITUENTS AT HIGH TEMPERATURES

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INTRODUCTION

Only a few methods are available for measuring the activities of alloy components at high temperature. Those most widely used consist in measuring equilibrium with a gas phase by transference experiments or with a liquid phase by distribution experiments, but there are many cases in which these are unsuitable or unduly cumbersome. In order to determine activities in alloys at high temperatures in such cases we have used two methods for measuring vapour or reaction pressures.

I. EFFUSION METHOD

This consists in measuring the molecular flow of a gas through an opening which must be wide and short in comparison with the mean free path. The method is therefore restricted to systems in which no constituent has a pressure exceeding about 0.1 mm mercury. The equipment commonly used consists of a small crucible with a lid carrying a hole of appropriate dimensions and exactly known cross section. The crucible is heated in a good vacuum and the amount of substance evaporating in a given time found either by determining the weight loss of the crucible or by condensing a defined fraction on a cooled condenser opposite to, and some distance from, the hole in the crucible lid.

Most of our activity measurements by this method concern aluminium in alloys containing mainly iron and aluminium; in addition silicon is present as a minor constituent (among others) and at the experimental temperature its volatility is sufficient for the loss in weight of the crucible not to be equivalent to the rate of aluminium evaporation. Furthermore, the weight of material evaporating is very small if alloys containing a relatively low proportion of aluminium are used; this makes the weight loss unreliable, and also makes it necessary to condense the total amount of aluminium evaporating.

The arrangement used at 1300°C (see Fig. 1) consisted of crucibles (a) and crucible lids (b) made from alumina or preferably beryllia. The hole in the crucible lid was ground to give as sharp an edge as possible, the cross section being measured by projecting the hole with a known magnification on to squared paper. The lid was fixed on the crucible by a molybdenum cap (c). In order to determine the small amount of aluminium effusing a small molybdenum funnel (d), closed by a molybdenum cap (e), was positioned on the top of the crucible lid but not tightly joined to it. Inside this funnel was another one (f) with lid (f') made of platinum. By this arrangement it is possible to collect practically the whole of the effusing vapour by absorption in

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the platinum parts of the funnel. Platinum was chosen for this purpose because it is much more efficient in absorbing aluminium vapour than for instance molybdenum. The funnel also has the advantage of avoiding the steep temperature gradient in the crucible which occurs if the crucible lid is freely radiating against a cooler surface.

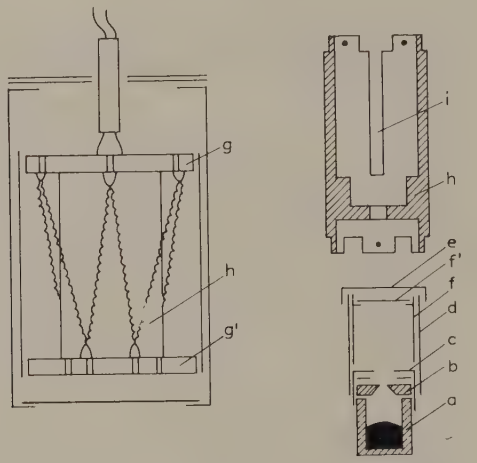

Fig. 1.

The crucible and funnel were placed in a small electric furnace suspended in a bulb joined directly to a high speed oil diffusion vacuum pump. The furnace is schematically shown in the figure, and consists essentially of two washer-like alumina rings (g, g'), which support the molybdenum resistance wire and are separated from each other by a molybdenum block (h) drilled along its axis to take the crucible and funnel and provided also with a slot (i) to take a thermocouple.

The aluminium content was determined, after dissolving the funnel and lid, by precipitating the aluminium together with a known amount of added iron and chromium as hydrated oxides, redissolving the precipitates, and comparing spectrographically the aluminium content of the solution with the iron content.

II. CAPILLARY VESSEL METHOD

This method was devised for measuring higher pressures. It permits the measurements of reaction or vapour pressures which are greater than about 1 mm. In the capillary vessel a heterogeneous equilibrium is established in which the substance of unknown activity participates and determines the pressure of one or more constituents of the gaseous phase. Another known equilibrium which does not interfere with the first one and which leads to a defined partial pressure in the gas phase is also allowed to establish itself in the vessel. A small sample of the gas mixture generated within the vessel is continuously allowed to escape from the vessel by laminar flow through

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a capillary opening in the vessel. There is therefore no restriction on the pressure of any constituent provided that the total pressure and the dimensions of the capillary are related to each other so that the flow through the capillary is (at least) laminar and that the amount of any constituent escaping does not noticeably change the composition of the reaction mixture. The vapours are condensed and analysed to establish the composition of the gas mixture in the vessel. The unknown pressure or pressures can then be derived from the analysis and the known pressure.

The method was originally[1] applied for measuring the aluminium monochloride pressure in the reaction:

$$\text{NaCl (solid or liquid)} + \text{Al (liquid)} = \text{Na (vapour)} + \text{AlCl (vapour)}$$

by comparing it with the saturation vapour pressure of sodium chloride on the basis of the analysis of the condensate for aluminium and sodium chloride. In this case and others) it was possible to choose for the second equilibrium a reaction in which the pressure had about the same temperature dependence as the first one, so that the results are only a little influenced by temperature fluctuations or by uneven temperature distribution which is especially important at high temperatures. During the last ten years the capillary vessel method has been applied in this Institute for the determination of the activities of the constituents of various alloys. Vessels made from graphite and alumina have been used. At present experiments are being made to investigate whether the method can be used for determining the carbon activity in alloys of iron and chromium at temperatures exceeding 1600°C. The reaction chosen is the reduction of magnesia by carbon and the reaction pressure of the magnesium is compared with the vapour pressure of chromium over the alloy. It has been possible to make the vessel and stopper from magnesia so that interference from any side reaction with the container material is excluded.

ACKNOWLEDGEMENTS

We are grateful to all our sponsors who supported the work in which these methods have been developed, in particular Aluminium Laboratories Ltd., Montreal, European Research Associates, Brussels, and International Alloys Ltd., Aylesbury, Bucks.

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HIGH TEMPERATURE MECHANICAL WORKING OF ARC-CAST MOLYBDENUM*

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INTRODUCTION

This paper discusses a number of aspects of the high temperature mechanical working of arc-cast molybdenum. Much of the subject matter is probably equally applicable to the working of a number of other high melting point metals.

In metallurgical practice metals are mechanically worked for a number of reasons. Firstly, they may be worked in order to shape them, this being especially true in the case of metals such as molybdenum which are not available in the form of shaped castings. Secondly, and perhaps more important, they are worked in order to remove coarse as-cast structures and inhomogeneities and to improve properties. Again in established metallurgical practice these objectives are achieved in the main by hot working, *i.e.* working at such a temperature that simultaneous recrystallisation takes place and the hardness remains essentially unaltered after working. To achieve this objective of hot working, a temperature of around 80% of the melting point is conventionally used. We immediately see then that by analogy with other metals we should be seeking to work molybdenum at a temperature of about 2100°C.

Some of the objectives of hot working set out above can be achieved by cold working followed by heat treatment, but it is not always possible to do this without cracking and rarely is the result so satisfactory. An important consideration in large-scale working operations is the ease with which the material can be deformed, and if we are seeking to develop metals or alloys to operate at temperatures of 1200°C or above then we must accept the fact that they will be stiff to work at these temperatures.

Molybdenum ingots have a large, oriented, type of grain structure. The problem is to remove all vestiges of this structure, and all the impurity concentrations existing at the large columnar grain boundaries. In addition a uniform fine grain structure is desirable.

If the definition of hot working given above is applied, then the hot working temperature range for molybdenum commences at about 1750°C, and below this we are cold working, or as it is commonly called, warm working.

The earliest attempts to warm work arc-cast molybdenum in A.R.D.E. were not successful due to a fairly high level of impurity content combined with a large grain size. It is interesting to note that warm working has been practised with sintered molybdenum, although of inferior purity, for many years. This is almost certainly due to the very fine grain size of this material. Improvements in de-oxidation resulted in the ability to warm work molybdenum, and at the present time the metal can be

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worked without serious risk of cracking in the temperature range 1000–1400°C. The development of true hot working is, however, still felt to be important because warm working does not appear to remove completely the influence of the columnar grain boundaries. Apart from this, the advent of higher strength molybdenum alloys will necessitate the use of higher temperatures whether warm or hot working is involved.

EQUIPMENT FOR HOT WORKING

All types of hot working operations have certain features in common. Heating furnaces are required and suitable materials must be available for handling tools and for rolls, dies or other components which have to come into contact with the hot metal. Present trends towards the solution of these problems are discussed below.

(*a*) *Furnaces*

Quite apart from the need to avoid contamination which will be discussed later, molybdenum must be heated in a non-oxidising atmosphere to avoid catastrophic oxidation. Fortunately the metal is not adversely affected by hydrogen and this forms a satisfactory furnace atmosphere.

It is possible to construct, with available materials, a refractory lined resistance type furnace with hydrogen atmosphere suitable for heating large billets of molybdenum to a temperature of about 1900°C. In one typical laboratory furnace in A.R.D.E. pure alumina bricks of 2 inches thickness are used to form a 4-inch square chamber 4 feet long and are surrounded by 4 inches of insulating brick. This furnace has 4 molybdenum rod elements $^1/_4$-inch diameter, recessed into the sides of the chamber. A uniform hot zone about 1 foot long is obtained and at 1800°C the power requirement is about 20 kW. Due to the large increase in the resistivity of molybdenum with temperature, it is necessary to raise the applied voltage during heating, and this is done automatically as a part of the control system, enabling the current to be held at any value up to 650 A.

An essentially similar furnace has been built and operated by the Tube Investments Technological Centre. This furnace uses rod elements $^1/_2$ inch in diameter and has a chamber 18 inches long by 6 inches square. The power consumption is about 20 kW at 1900°C.

Previous to the use of these high temperature resistance furnaces, it was common to heat molybdenum to a maximum of 1280°C in barium chloride salt baths. In America heating in such a salt bath has been followed by a short period of heating in a high frequency coil up to 1450°C.

Temperature measurement in these furnaces can be made with a Pt–20% Rh/Pt–40% Rh thermocouple or by the use of an optical pyrometer.

(*b*) *Tools and handling*

In rolling or extruding molybdenum at 1800–1900°C, it is apparent that the limit of steel rolls or dies is being reached. It must be remembered that molybdenum is cast into water cooled copper moulds successfully because of the rapid chilling, and that similarly molybdenum can be worked at these high temperatures without melting the tools, provided the relative masses are favourable and that the contact times are short. Handling tools of small mass present something of a problem, and in general

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it is advisable to make these of molybdenum itself or to use molybdenum inserts or coatings.

Because of its low specific heat and high thermal conductivity molybdenum cools very rapidly on removal from the furnace. Measurements have shown that the temperature at the centre of a 1⅝-inch diameter ingot falls from 1600°C to 1400°C in 20 seconds. It is, therefore, necessary to ensure short transfer times from furnace to working equipment, and frequent repeats are required.

It would be expected that lubricants would have a considerable influence on tool and die wear. In much of the early working, particularly extrusion of molybdenum the Ugine-Sejournet technique with a molten glass lubricant was adopted. This worked satisfactorily up to about 1400°C provided that leaded glasses were avoided. More recent work, and particularly higher temperature work has tended to adopt graphite or aluminium greases as lubricants. Lubricants of similar types are used in forging.

Although rolling, forging and extrusion have been carried out at 1900°C with conventional steel tools, there is little doubt that for large-scale industrial operations at these temperatures significantly better materials would be required.

METHODS OF WORKING

Molybdenum has been rolled, forged and extruded at temperatures up to 1900°C. Before describing some of the metallurgical results of these operations mention should be made of two forgeability or workability tests which have been adopted. In the first of these tests, described by HUGHES[1], a specimen is subjected to a hot torsion test. The number of twists to fracture at any temperature gives an indication of the feasibility of extrusion at this temperature. The torque is measured and its value at any temperature gives an indication of the pressure required for extrusion. Tests on molybdenum have normally been carried out in hydrogen atmospheres and have indicated that the extrudability should increase with temperature up to 1900°C, the highest temperature of test. The torque values indicate that at 1600°C molybdenum requires extrusion pressures similar to those used for austenitic stainless steels at 1250°C.

An interesting observation was made in this test of the effect of oxygen and nitrogen. Introduction of these gases in place of hydrogen for only 30 seconds prior to testing resulted in a large decrease in the number of twists to fracture.

In early work in A.R.D.E. an upset forging test was adopted. This test has been extensively used by the Climax Molybdenum Company in America, and has generally indicated decreasing forgeability at temperatures above 1200°C. These tests have been carried out in air, however, and therefore are not strictly comparable with the torsion tests, which, when carried out in hydrogen, are more a test of inherent workability than of forgeability in air.

(a) *Rolling*

A considerable amount of experimental rolling has been carried out by A.R.D.E. starting with ingots up to 2½-inches diameter and using rolling speeds of 50 feet per minute. The effect of rolling temperature on the breakdown of the cast structure is shown in Fig. 1. The bars have been given 50% reduction in area in three passes, without any reheating except in the final bar, which had 5 minute reheats at 1800°C.

The bar rolled at 1800°C with re-heats is the only one showing extensive recrystalli-

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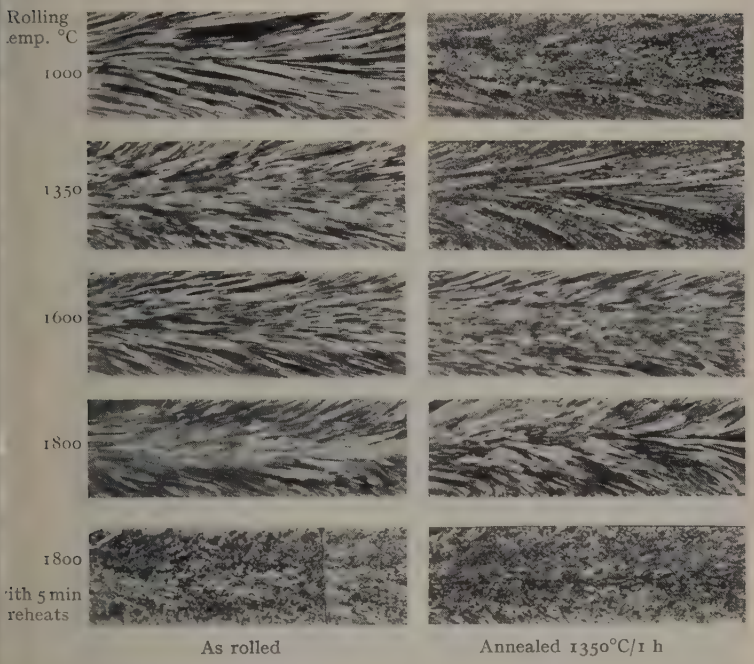

Fig. 1. Macrostructures of Mo–0.01% C arc-melted ingots rolled at various temperatures (50% R.A. in three passes, without reheats).

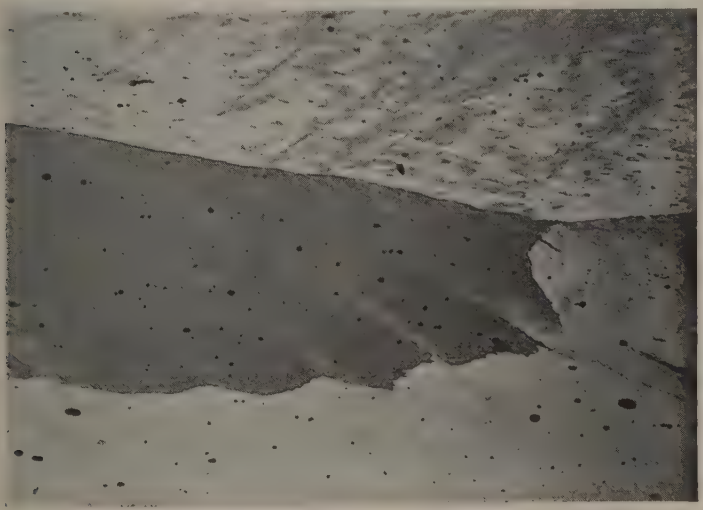

Fig. 2. Microstructure of the bar rolled at 1350°C (× 150).

sation in the rolled condition, and the original structure is almost completely lost. Th bar rolled at 1600°C has slight recrystallisation close to the surface after annealing Bars rolled at 1350°C and 1000°C show appreciable recrystallisation after annealin at 1350°C for 1 hour, but the structures are very non-uniform, and the original ingo

Fig. 3. Microstructure of the bar rolled at 1350°C and annealed at 1350°C for 1 hour (× 150).

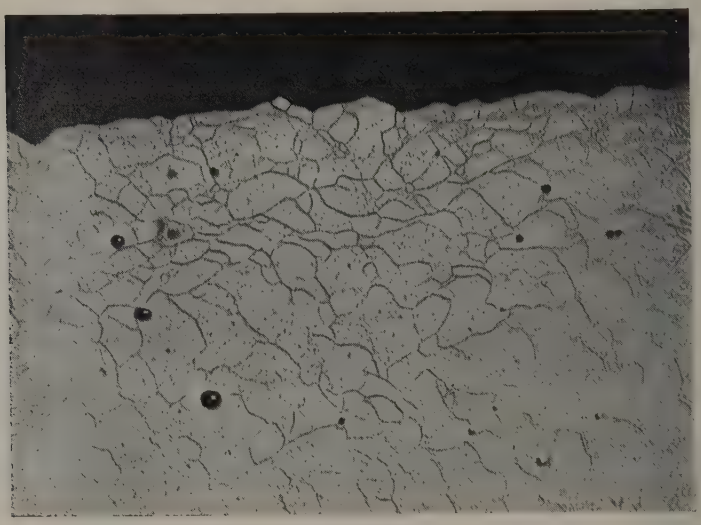

Fig. 4. Sub-structure in the bar rolled at 1600°C and annealed at 1350°C for 1 hour (× 706).

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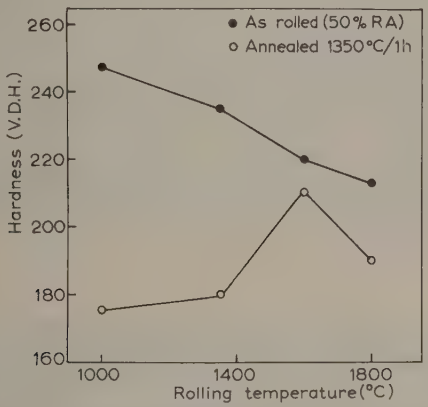
rains are clearly visible in places. Figs. 2 and 3 show the microstructures of the ingots olled at 1350°C before and after annealing.

Fig. 4 shows sub-structures in the 1600°C rolled ingot after annealing at 1350°C. t seems that this type of structure occurs when there is insufficient strain in the ma-erial to cause complete recrystallisation.

In Fig. 5, a graph of hardness against rolling temperature, it is shown that in ingots olled at 1000°C and 1350°C there is considerable work hardening and that annealing auses softening corresponding to complete recrystallisation. Working at higher tem-eratures causes less hardening and less change in hardness on annealing. The change hardness in these ingots is caused by stress relief and a certain amount of recovery s illustrated in Fig. 4.



g. 5. Hardness of Mo–0.01% C bars, as rolled (50% R.A. in three passes without reheats), and after annealing at 1350°C for 1 hour.

Extrusion

This process has been commonly used in America for primary breakdown of cast gots. Extrusion of billets weighing up to 1,200 lbs. is carried out at about 1300°C. Little work has been reported in this country, but in recent years high temperature xtrusion studies have been carried out at the Tube Investments Technological Centre t Walsall. In this work 4-inch billets have been extruded with a 5:1 extrusion ratio t 1500°C and 1800°C using an 800 ton press.

The leading end of the 1800°C extrusion has a very mixed grain size in which certain rains or grain boundary regions are recrystallised and large areas show a sub-struc-ure; these latter regions are deformed but not recrystallised. At the middle and rear f the extrusion the proportion of recrystallised grains progressively increases. The ecrystallised grain size decreases from front to back. Similar general effects are observ-d in the 1500°C extrusion, but the proportion of recrystallised grains is higher. The .S.T.M. grain sizes are 4, 6, 8 and 6, 7, 8 for front, middle and back of the 1800°C nd 1500°C extrusions respectively. Figs. 6 and 7 show the microstructures near the entre of the 1800°C and 1500°C extrusion.

It appears that at high temperatures certain grains may deform and recrystallise adily, thereby perhaps preventing extensive deformation of the less favourably

eference p. 124

oriented grains. The most uniform microstructure obtained was at the rear end o the 1500°C extrusion, where there remain only a few elongated fragments of the original structure.

Fig. 6. Centre of bar extruded at 1800°C with a 5:1 extrusion ratio (× 150).

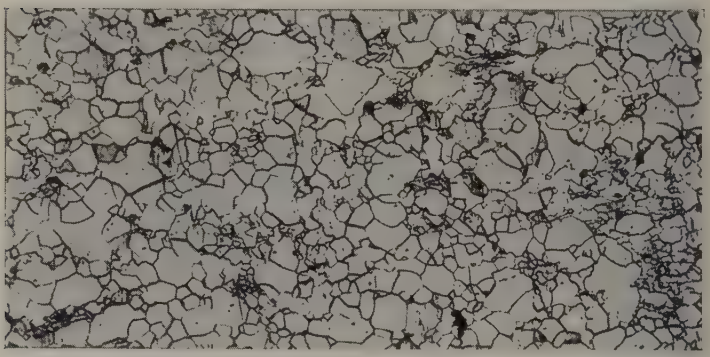


Fig. 7. Centre of bar extruded at 1500°C with a 5:1 extrusion ratio (× 150).

PROPERTIES

When rolling is carried out all at one temperature, the rolling temperature appea to have an important influence on the mechanical properties. When rolling is carri out over a range of temperatures, both starting and finishing rolling temperatur appear to be important.

Fig. 8 shows the tensile strength and elongation of 1/4-inch strip rolled at vario temperatures with 30% reduction per pass, and with re-heats between passes. All tl material was initially broken down by rolling at 1350°C. There is a progressive r duction in strength with increase in rolling temperature in line with the hardn

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results, and an increase in ductility between 1000 and 1350°C followed by a sharp drop at 1600°C. The data for bars extruded at 1500°C and 1800°C agree well with that for rolled material.

With an initial rolling temperature of 1350°C, improvements in ductility and toughness result from finishing at lower temperatures. This is shown particularly by a progressive fall in the slow bend transition temperature from —10°C for material finish rolled at 1350°C, to —70°C for material rolled at 600°C.

There is little quantitative information available on the effect of working temperature on properties, but one general observation in all the A.R.D.E. work on rolling at high temperatures is that there is an increasing tendency to surface cracking with rolling temperatures between 1400°C and 1800°C. Fig. 9 shows an example of this cracking in a bar rolled from 1800°C. These cracks, although they appear severe, do

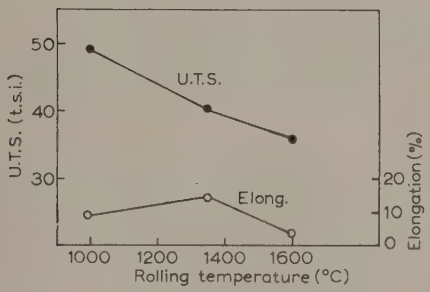

Fig. 8. Tensile properties of 1/4-inch Mo–0.01% C strip in the as-rolled condition

Fig. 9. Surface cracks on a bar rolled at 1800°C (× 50).

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not penetrate very deeply and are intergranular in nature. It seems likely that this cracking results from atmospheric contamination, and this problem is discussed in the next section of this paper.

ATMOSPHERIC CONTAMINATION

Heating of molybdenum for forging must be done under non-oxidising conditions, and in practice a hydrogen atmosphere has generally been used. It has not, however, been practical to attempt to protect the material during the out-of-furnace time. There is very little data on contamination of molybdenum by exposure to air, but it has been shown that oxygen penetration can take place to a depth of about 0.025 inch during the course of a fairly prolonged forging operation, with re-heating in a supposedly neutral gas atmosphere. A further piece of evidence obtained in some American work was that the oxygen content of thick sheet material, worked from arc melted ingot, can increase by a factor of approximately ten as a result of the various operations performed on it.

Contamination is probably the most serious single problem preventing the development of improved hot working methods for molybdenum and several other metals. Similar problems have arisen with other lower melting point metals of high reactivity and here the solution has been to work in a can. This solution would have been adopted for molybdenum had there been any suitable canning material available for working at temperatures above 1400°C. The limited amount of work carried out has been with stainless steel cans at temperatures of 1300°C and with chromium plating at 1600°C. The chromium plating certainly reduced the amount of surface cracking and is a possible solution at this temperature. No solution on these lines can be foreseen for temperatures appreciably higher than 1600°C however.

There have been several attempts to conduct forging and rolling operations under completely inert atmosphere conditions, but so far there is little evidence that this approach has been really successful for hot working of molybdenum. The answer may well be that sufficient purity of the atmosphere has not been achieved. This approach has considerable potential and may be developed further. There is under construction in America a large argon atmosphere process laboratory for working a number of impurity sensitive metals. The ideal atmosphere for this purpose would be hydrogen, but the explosion risks with a large quantity of hydrogen and high temperature furnaces and metal are so serious as to make this approach quite impracticable.

If no other solution can be found it is likely that future progress will be along the lines of completely new metal working processes, involving heating and working as a closely combined sequence of operations, carried out in the same piece of equipment and using small hydrogen atmosphere enclosures. It is easy to envisage this type of operation being carried out by hammer or press forging for example.

In conclusion, it seems probable that, although reasonably good properties can be obtained by warm working, it will become necessary in the future to hot work molybdenum alloys at around 2000°C under truly inert conditions, and that when this is achieved, superior properties will result. At the present time the problems of working at up to 1900°C are being solved, but contamination remains as a serious disadvantage, preventing the full realization of the benefits of hot working.

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TECHNIQUES FOR CREEP TESTING AT HIGH TEMPERATURES

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INTRODUCTION

It is the purpose of the present contribution to describe some of the experiments which have been carried out at the National Physical Laboratory to develop techniques for creep testing metals and cermets at high temperatures. The development of these techniques is not complete but it is hoped that the results described will be of interest to those who propose to enter this field of testing.

TESTS ON CERMETS

Initially it was required that cermets should be tested at temperatures of 1000°C and above. These materials are very brittle and the only practical process for shaping them was by grinding with a diamond wheel. In consequence a design of test-piece with conical ends shown in Fig. 1 was used, which had a gauge length of 1.5 inch, a diameter of 0.15 inch and overall length about 3 inches. The diameter of the ends was $^5/_8$ inch. For tests at 1000°C it was considered that Nimonic 80A would be suitable

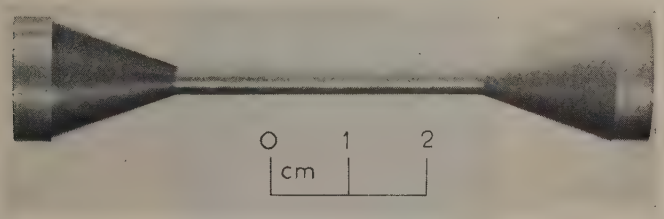

Fig. 1. Cermet test-piece.

for grips and pull rods. The apparatus is shown in Fig. 2 where it can be seen that the conical ends of the test-piece are held in four jaw collets of Nimonic 80A. The strain of the test-piece was measured by attaching to the grips a conventional mirror type creep extensometer with 80/20 nickel-chrome limbs. The test-piece grips were made sufficiently massive to ensure that the majority of creep strain occurred within the gauge length of the test-piece; the dimensions used gave a 16 to 1 ratio of stress in test-piece to the stress in the grips. It was also considered desirable to adopt a design which could be made subsequently in a ceramic material. Tests were carried out with

the Nimonic apparatus at 1000°C for times up to 1000 hours and stresses on the test-pieces of up to 12,000 lb./sq.in. At operating temperatures of 1000°C, errors in strain measurement must have resulted from the observed bedding down of the collets and the probable circumferential creep of the cylindrical adaptor, which would tend to increase the apparent strain. These errors, however, were offset by the extension of the limbs under their own weight to the extent of 10^{-6} in./in./h. These errors would probably be reduced by using more advanced high temperature resisting materials.

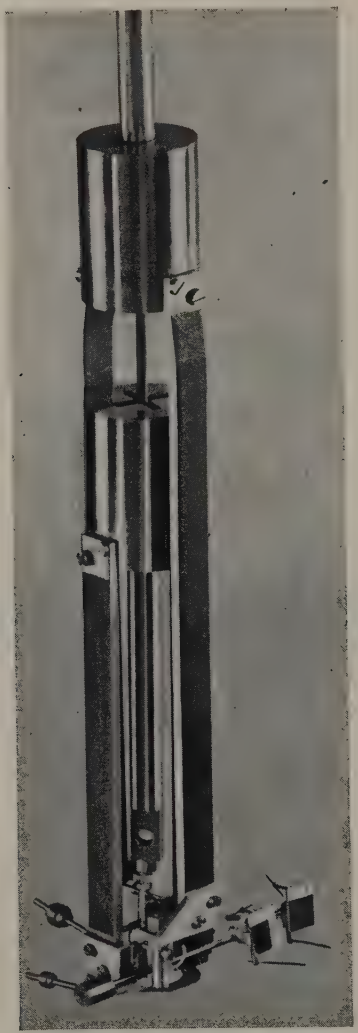

Fig. 2. Nimonic creep adaptors for tests up to 1000°C.

Grips were made from 20% $Fe-Al_2O_3$ cermet to the original design, but without the extensometer fittings, in an attempt to achieve higher testing temperatures. A test was carried out at 1200°C and 5000 lb./sq.in. on a 20% $Fe-Al_2O_3$ test-piece for about 1300 h using these cermet grips. An attempt to determine the extension of the test-piece was made by measuring the fall of the loading lever of the creep machine with a dial gauge. However, these measurements were obscured by the increase in volume of the cermet as the result of oxidation of the iron it contained. At the end of this test it was found that all the mating surfaces had sintered together and the assembly was broken during the removal of the test-piece.

An alternative set of grips, including extensometer limbs, was made by K.L.G. Plugs Ltd. to a design from the National Gas Turbine Establishment. These grips were constructed from "Hylumina" fired at 1600°C. This arrangement, shown in Fig. 3, employed the same test-piece form, with conical ends, held as before in split collets.

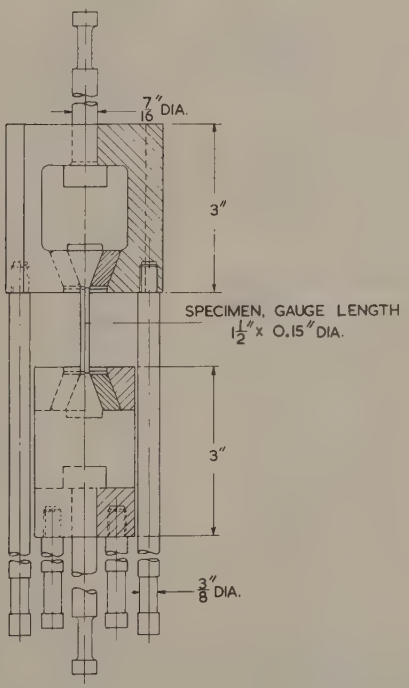

Fig. 3. Ceramic creep adaptors and extensometer legs.

The extensometer legs also of the alumina material were screwed into the grips. The rhombs and mirrors of the extensometer were clamped on to the lower ends of the legs. This apparatus was used for a test at 1400°C and at a stress of 1000 lb./sq.in. on a test-piece of 20% $Cr-Al_2O_3$ but failure of one of the pull rods occurred after a few minutes when carrying a stress of only about 120 lb./sq.in. It was found also that

the mating surfaces had sintered together. The pull rod had been sintered from an extruded compact whereas it is believed that a hydrostatically prepared compact would have been stronger.

At this stage it seemed unlikely that ceramic or cermet grips and extensometers could be used for any adequate length of time at temperatures of 1200°C and above. A fresh approach to the problem was made by using a test-piece which would protrude from each end of a small furnace surrounding the gauge length. In this way a relatively cool attachment could be made to the test-piece, with Nimonic 80A grips, outside the furnace. Fig. 4 shows the test-piece and grips for this testing technique. The shape

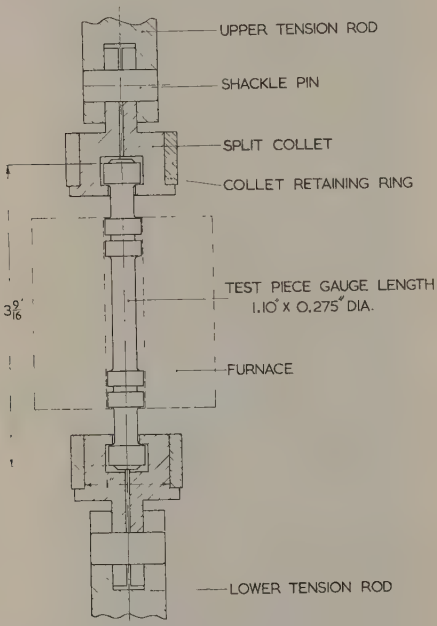

Fig. 4. Specimen and grips for high temperature creep testing.

of the new test-piece was designed to be easier to manufacture than the conical ended one, previously used, as the blank could be ground between centres using a cylindrical diamond wheel set at right angles to the axis of the test-piece. The larger diameter of the gauge length, 0.275 inch, compared with 0.150 inch for the conical test-piece, reduced the risk of breakage during manufacture, required a smaller diameter of blank, and gave a larger volume of material in the gauge length. The ends of the test-piece were held by Nimonic 80A collets split into two halves to engage the shoulders on the test-piece, the two halves of the collets being held together by cylindrical collars. Pin joints were provided to give some degree of axiality of loading and the assembly was mounted in a Dennison T.47 creep machine, of 3/4 ton capacity. The strain in

the gauge length was determined by measuring the fall of the loading lever of the machine with a dial indicator to an accuracy of about 0.1 per cent strain.

The furnace, shown in Fig. 5, had a winding of 18 s.w.g. (0.048 inch) diameter of platinum–10% rhodium wire mounted on the inside of an alumina tube with an alumina cement. Most of the turns of this winding were concentrated near each end of the tube and a single turn in the central region. The winding was thermally insulated by fine alumina powder contained in a stainless steel cylindrical case having pyrophyllite ends. A sighting tube was inserted radially to allow temperature measurements to be made on the gauge length with an optical pyrometer. It was found by inserting in the fur-

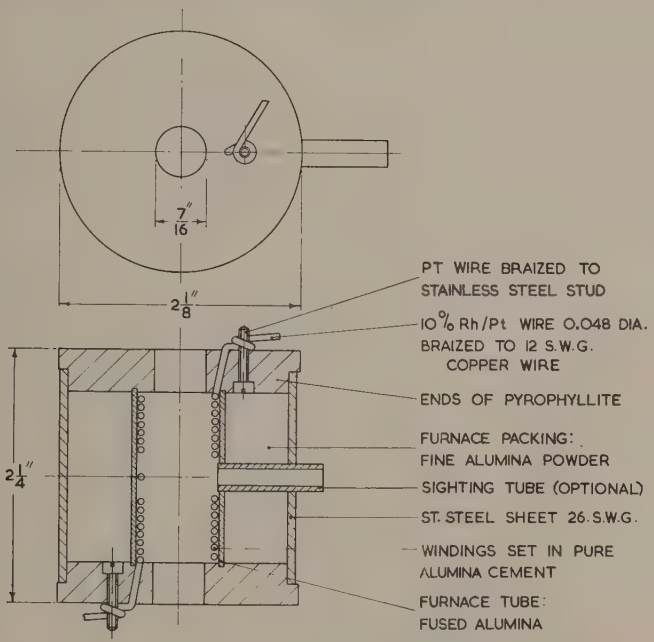
7/16"
2 1/8"
2 1/4"
PT WIRE BRAIZED TO STAINLESS STEEL STUD
10% Rh/Pt WIRE 0.048 DIA. BRAIZED TO 12 S.W.G. COPPER WIRE
ENDS OF PYROPHYLLITE
FURNACE PACKING: FINE ALUMINA POWDER
SIGHTING TUBE (OPTIONAL)
ST. STEEL SHEET 26 S.W.G.
WINDINGS SET IN PURE ALUMINA CEMENT
FURNACE TUBE: FUSED ALUMINA

Fig. 5. Furnace for high temperature creep testing.

nace a dummy cermet test-piece containing a hole in the centre of the gauge length (0.1 inch diameter by 0.2 inch depth) that the difference in appearance between this hole and the surface of the test-piece was negligible at 1400°C, *i.e.* approximately full radiator conditions were obtained at this temperature. Alternatively, temperatures were measured by 0.2 mm diameter Pt–Pt/13% Rh thermocouples sheathed in fine alumina tubing. Since the test-piece was a close fit in the ends of the furnace to minimise heat losses, longitudinal slots were cut in the shoulders of the test-piece to make room for the thermocouples. The beads of the thermocouples were covered with platinum foil radiation shields and were tied on to the gauge length with platinum wire. Thermocouples would be expected to be less suitable than optical methods for measuring

temperatures above 1200°C due to the possibility of contamination and deterioration of thermocouple materials and of the decreased insulating properties of the alumina sheathing. Power was supplied to the furnace winding from a suitable transformer, 20 A at 15 V being sufficient to maintain 1450°C.

The temperatures at the centre of the gauge length were higher than at the ends. The gradients were not reproducible from one furnace to another and could not be reduced to a satisfactory level at 1400°C. Attempts to improve these gradients were confined to the tests in vacuo and are described below. A test result obtained with this assembly is shown in Fig. 6. This is a creep curve of 20% $Cr-Al_2O_3$ cermet obtained at 1400°C and at a stress of 2000 lb./sq.in.

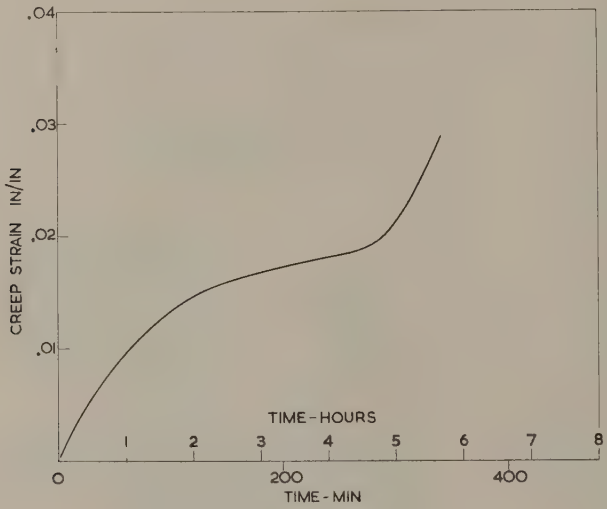

Fig. 6. Creep curve of 20% $Cr-Al_2O_3$ obtained at 1425°C and 2000 lb./sq.in.

TESTS ON REFRACTORY METALS

The apparatus for testing ceramics was modified to test refractory metals by enclosing the test-piece, furnace and grips in an evacuated vessel. A sketch of the apparatus for testing under vacuum is shown in Fig. 7. The vessel was carried by the lower pull-rod whilst the movement of the upper pull-rod, relative to the vessel, was permitted by use of a metal bellows. The effect of atmospheric pressure on the pull-rod and bellows was balanced out on the creep machine. Grips and pin joints within the vessel were similar to the apparatus for tests in air. The upper and lower pull-rods and the vessel casing were water cooled. Temperatures were measured either with an optical pyrometer sighted on to the centre of the test-piece, through the window in the evacuated vessel and the sighting tube in the furnace, or by thermocouples insulated with alumina tubing. The fine thermocouple wires from the test-piece were soldered to a connector strip inside the evacuated vessel and stouter Pt–Pt/13% Rh wires led through lap joints in the large "O" ring on the base plate. Current for the furnace

was led through connectors in the base plate which were insulated from the base plate and made vacuum tight by "O" rings. The initial experiments were carried out using the same furnace as was used for the air tests. The alumina insulating material in this furnace necessitated rather long pumping times but nevertheless pressures of about $5 \cdot 10^{-4}$ mm Hg were obtained at 1100°C.

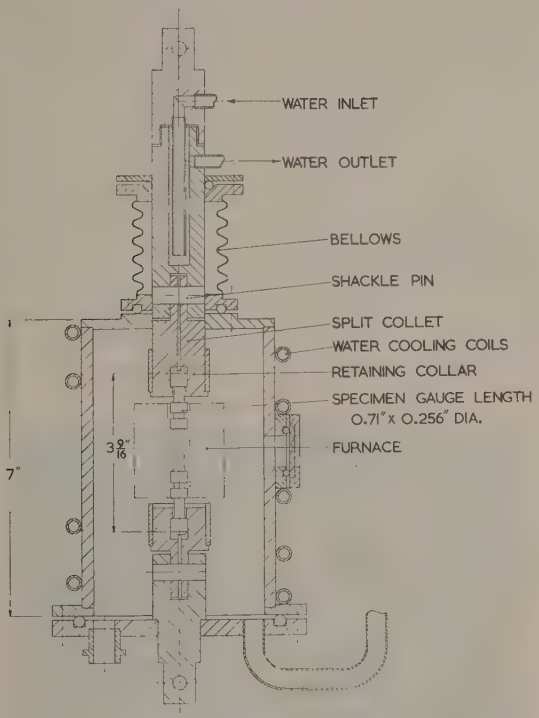

Fig. 7. Apparatus for creep testing in vacuo at high temperatures.

Modifications to the furnace design have been made and tests carried out for times up to 300 h at 1100°C. Temperature gradients along the gauge length were about 20°C but later work has shown that these may be reduced to 7°C or less. The modifications included various arrangements of the furnace windings and the electrical circuits supplying and controlling the power. A reduction of pumping times has been obtained by the use of radiation screens in place of alumina packing.

ACKNOWLEDGEMENTS

The work described has been carried out as part of the research programmes of the National Physical Laboratory and of the Mechanical Engineering Research Board of the Department of Scientific and Industrial Research on behalf of the Ministry of Supply. This paper is published by permission of the Ministry of Supply and of the Directors of the National Physical Laboratory and of Mechanical Engineering Research.

PRELIMINARY OBSERVATIONS ON METHODS OF MEASURING MECHANICAL PROPERTIES OF SOLIDS AT HIGH TEMPERATURES

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The advent of the gas turbine, rocket propelled aircraft and missiles has forced the engineer to develop new materials to withstand the high temperature and stresses imposed by such propulsive devices. The use of nuclear energy also meant that new materials to withstand extreme temperatures were needed. The materials which have assumed importance are the carbides, borides, nitrides, refractory metals and hybrid materials such as cermets and metals reinforced with refractories.

At Cambridge during the last few years a small research group under the direction

Fig. 1. General view of furnace.

of F. P. Bowden, has been formed for studying the properties of solids at very high temperatures.

The aspect of the work described here can be divided into parts:

(1) The investigation of the tensile strength of refractory metals of temperature up to ca. 2500°C.

(2) The measurement of the coefficient of friction of metallic carbides and its variation with temperature.

The furnace used for these experiments was a carbon tube resistance furnace (Fig. 1).

The choice of carbon as the resistor material was made because of its excellent high temperature properties. The coefficient of thermal expansion is low and consequently results in dimensional stability. It has a high mechanical strength and retains it at high temperatures even under load. Low elastic moduli and high thermal conductivity, combined with a low coefficient of thermal expansion give it a high resistance to thermal shock.

The main disadvantage in using carbon is that it has a high vapour pressure. At high temperatures carbon vapour is present in sufficient quantity to react easily with

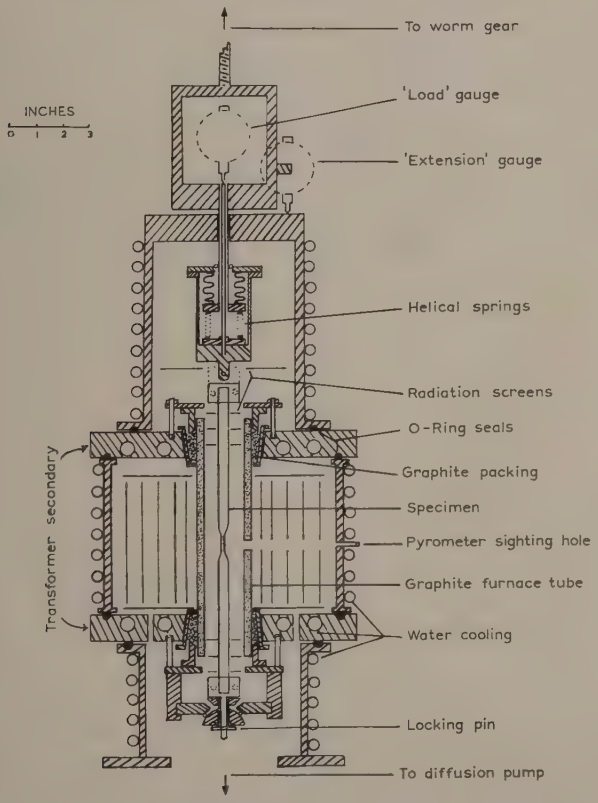

Fig. 2. Vacuum furnace for high temperature mechanical tests.

the specimens under examination. The reaction between carbon vapour and refractory metal limits the upper temperature for metal work to just above 2100°C. Carbon tube furnaces can be operated as vacuum furnaces (0.1 μ) only up to about 2200°C. Above this temperature it is necessary to work under argon or another inert gas. Under such conditions carbon furnaces will operate at a temperature just exceeding 3000°C before carbon will evaporate off the furnace tube.

Carbides on the other hand tend to lose carbon when heated and consequently need to be heated in the presence of a carburizing atmosphere to suppress the decomposition of the carbide.

The main difficulty in undertaking mechanical tests in such a furnace is preventing the heat from impairing the measuring device. The essential components of the tensile head are shown in Fig. 2.

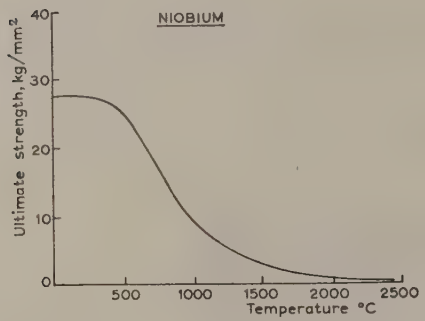

Fig. 3. Plot of U.T.S. *vs.* temperature for niobium.

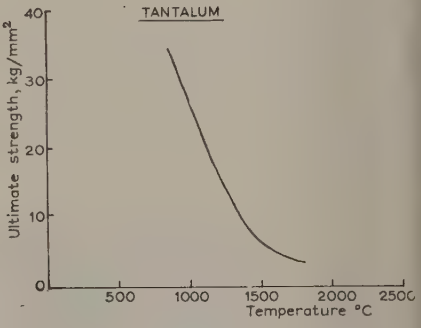

Fig. 4. Plot of U.T.S. *vs.* temperature for tantalum.

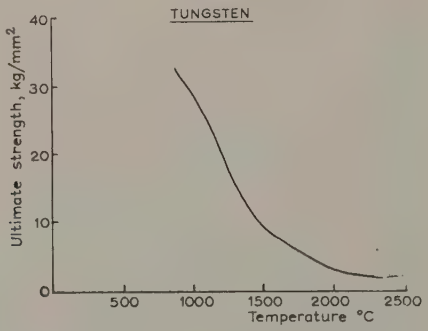

Fig. 5. Plot of U.T.S. *vs.* temperature for tungsten.

The specimens are in the form of strip and consequently the major heat transfer to the measuring portion occurs by radiation which is minimised by radiation shields. The metal strip is gripped between pyrophyllite slabs in steel chucks. The lower chuck is located in a swivel to ensure that the pull is always along the axis of the specimen. The upper chuck is fixed on to the spring device which is itself attached to a motor

driven carriage. The load is applied by driving the carriage upwards when a force is transmitted to the specimen through small helical springs. The extension of these springs gives a measure of the load applied. The total movement of the carriage is also measured and represents the sum of spring extension and specimen extension. With this information it is possible to plot load-extension curves and measure the ultimate tensile strength. Elongation must be measured from reference marks on the specimen.

Figs. 3, 4 and 5 show the results obtained for niobium, tantalum and tungsten. The material is received in the worked condition having been formed from sintered bars. The total impurity is stated as being less than 0.1%. The U.T.S. curves shown

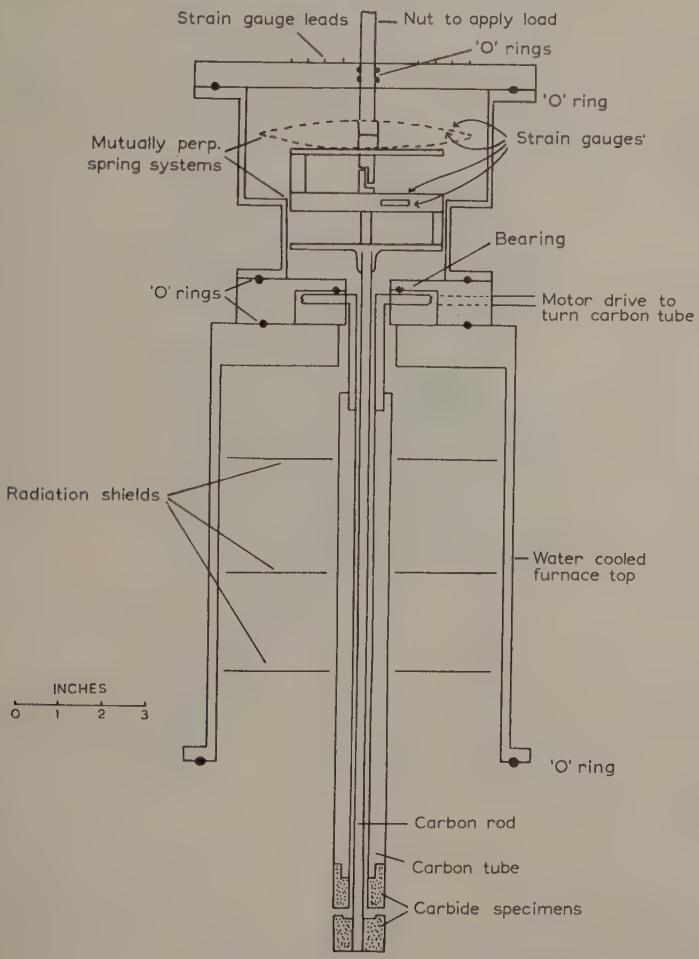

Fig. 6. Schematic drawing of friction apparatus.

are characteristic of recrystallisation curves. Work is at present in progress on the strength variation of recrystallised material.

The carbon tube furnace has limited the upper temperature so that for metal work two new types of furnace will be employed. The specimens will, if sintered strip, be heated in a radio frequency induction furnace using a metal tube as susceptor. An electron bombardment zone refining unit will be used if necessary to prepare single crystals of the above materials and then the "heater" adapted so that a zone can be heated to a constant temperature for mechanical testing.

An apparatus has been constructed for measuring the coefficient of friction at temperatures up to 2500°C and is shown in Fig. 6.

In this case cooling problems were much more acute as conduction through the rod and tube supporting the specimens was appreciable. This was remedied by an increased use of water cooling.

The principle of the apparatus is to rotate a carbide annulus and record the effect, that is the torque it produces when another carbide annulus is pulled with a known load into contact with it. The carbide specimens were pinned on to the rod and tube by carbon pegs (see Fig. 7).

Fig. 7.

The tube is rotated by a motor drive and the rod used to pull the two carbide specimens into contact. The normal load and torque are measured electrically by strain gauges as shown in Fig. 8.

The deflection of the bow springs is used to measure the normal load. The rotating carbide will tend to turn the carbide pulled into contact with it — the actual torque transmitted depending upon the normal load and the coefficient of friction. The torque causes a deflection of the flat springs and hence can be evaluated. The system has with a suitable selection of springs sufficient rigidity to measure high values of the

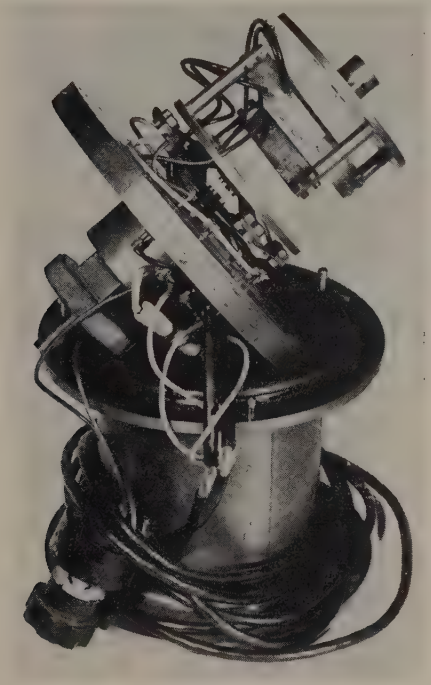

Fig. 8. Spring mechanism.

coefficient of friction and also the sensitivity to measure the lower values at lower temperatures. Strain gauges are very temperature sensitive and so to avoid spurious temperature effects two gauges were used to measure each of the loads. Each pair was fixed on to the same metal spring and connected into opposite sides of the bridge. This also served to double the sensitivity since when one gauge is stretched the other is compressed. The results for the dependence of friction on temperature for tungsten, boron and titanium carbides are shown in Figs. 9, 10 and 11.

The value of μ for the carbides increases with temperature. Unlike metals they do not seize after outgassing and have reasonably low values of μ above 1000°C. An interesting feature for the titanium and tungsten carbides is that they pass through a distinctive minima. The reason for this may be that weakening of the intercrystallite

forces occurs until the coefficient of friction decreases but at temperatures above 1200°C sintering is occurring and this process increases the friction.

Now that the various methods of heating are available — resistance, induction and electron bombardment — the scope of the work is being considerably widened. Apparatus

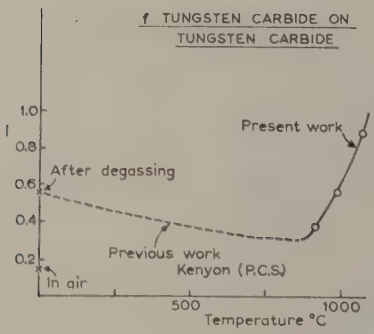

Fig. 9.

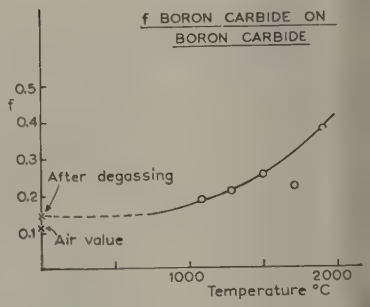

Fig. 10.

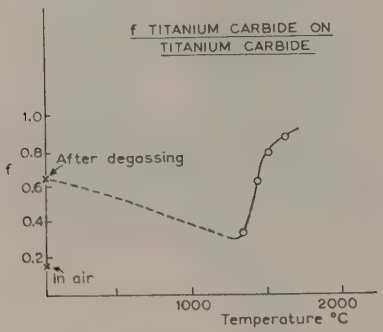

Fig. 11.

to measure hardness of carbides, borides etc. has been constructed and measurements are currently being attempted. An optical and X-ray microscope for temperatures up to 2000°C is under construction and it may be possible to increase this to 3000°C for selected substances.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. F. P. Bowden, F.R.S., for his interest and advice. They are also indebted to the Ministry of Supply and the Atomic Energy Authority, Harwell, for permission to publish the parts of the work sponsored by them.

THEORY OF THERMAL STRESSES*

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In the present paper we shall discuss an extension of the theory of thermal stresses which removes certain limitations of the simple theory. This extension was made in the first place to deal with problems involving graphite at high temperatures, but we are hopeful that the method will find application in the theory of the thermal fatigue of metals.

With simple theory one cannot estimate the effect of ductility of a material upon the thermal stresses which can be induced therein. This is because the simple theory assumes that the thermal conductivity, thermal expansion, Young's modulus, and Poisson's ratio are constants.

The extension which we shall describe is essentially a method of calculation of thermal stresses which allows all these so-called constants to vary with temperature and what is more important can cope with stress strain curves which bend over when plastic strain occurs.

We may outline briefly the method and the theory behind it and then give some results of its application to a simple problem involving graphite. We may then hope to learn, in the course of discussion, of aspects of the thermal stress theory of metals which may be profitably tackled in the same way.

This theory is essentially a method of calculation of thermal stresses which has been programmed for an electronic computer. It is assumed that, when we set out, we have data available on the thermal conductivity and thermal expansion *versus* temperature of the material and possess sufficient stress–strain curves at different temperatures so that given any biaxial strain at any given temperature we are able to find the corresponding stress.

We shall only discuss flat plates in which the thickness is small compared to other dimensions and in which temperature is a function of depth in the plate only. The treatment of some other simple shapes with simple temperature distributions is very similar.

It is convenient to think of the plate as comprising many thin laminations (Fig. 1). In the course of the theory we get from the initial unstressed state at uniform temperature to the final stressed state via several completely hypothetical states, rather in the way one calculates from thermodynamic data the heat absorbed in a complicated process.

Fig. 2 illustrates the original state of the section of the plate AA BB, uniformly at zero temperature and zero stress.

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Fig. 3 shows the final temperature profile established. At this hypothetical stage the laminae are allowed to expand freely, so there is no stress, while the section AA BB deforms as shown.

Next we compress the laminae back to their original lengths, maintaining the temperature profile. The compressive strain involved equals the natural expansion which is known and the temperatures are known, so the stress profile is calculable (Fig. 1).

Figs. 1 and 2.

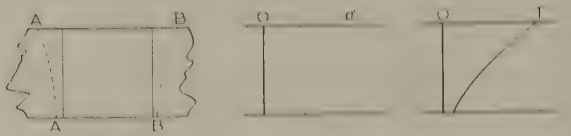

Fig. 3.

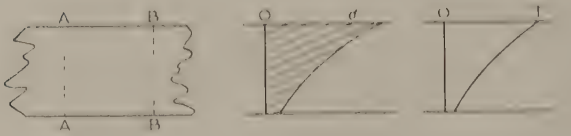

Fig. 4.

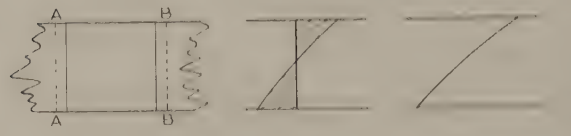

Fig. 5.

Fig. 6.

We must now consider what distortions of the section AA BB are in fact allowable and what conditions must be satisfied by the stresses. The plate is considered to have no lateral forces applied to its edges which implies that

$$\int_0^h \sigma \, dx = 0$$

wherein σ is the stress and x the distance from one face and h the thickness. Since the thickness of the plate is small compared to the other dimensions the plane sections AA′ BB′ must remain plane.

There are now two situations to consider: if the plate is prevented from bending

then the sections AA′ and BB′ must remain *parallel* which means that the laminae must all expand the same amount. If the plate is perfectly free to bend then there can be no bending moment *i.e.*

$$\int_0^t \sigma x \mathrm{d}x = 0.$$

Fig. 5 shows the type of distortion allowed in a plate which can not bend, and the effect upon the stress profile. If we make a guess at the amount $\Delta\varepsilon$ of the expansion, we know that the strain in each lamination is less than the natural thermal expansion by this amount and so the corresponding stresses can be calculated. According as $\int_0^t \sigma \, \mathrm{d}x$ is then found to be positive or negative we increase or decrease our first estimate of $\Delta\varepsilon$ and repeat until

$$\int_0^t \sigma \, \mathrm{d}x = 0,$$

then we have the right answer.

Fig. 6 shows the type of distortion allowed in a bending plate and the effect on the stress distribution. Now we adjust *curvature* of the plate according as $\int_0^t \sigma x \, \mathrm{d}x$ is positive or negative in addition to the first iteration.

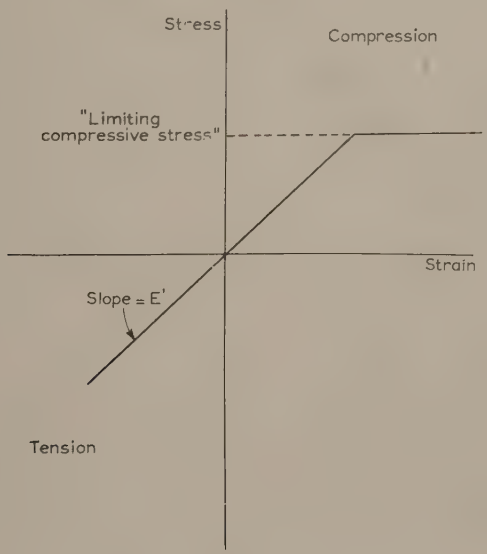

Fig. 7.

It remains to show some sample results. For the purpose of making plain the effect of ductility the stress strain curve has been idealised to that shown in Fig. 7, a curve

which is characterised by two parameters: the elastic modulus and the limiting compressive stress.

The data used for the calculations are shown in Figs. 8–11. The thermal conductivity varies over the chosen temperature range by a factor of more than 10. The thermal expansion is almost linear with temperature. The biaxial elastic modulus E', which is usually replaced by $E/(1-\mu)$ in the simple theory, is assumed to have a maximum value at about 2000° K. The limiting compressive stress is assumed to fall sharply with increasing temperature. The problem considered is that of a graphite plate in which a steady state of heat flow has been established with one face at 1500°K and the other at 3000°K (Fig. 14, upper pair of curves).

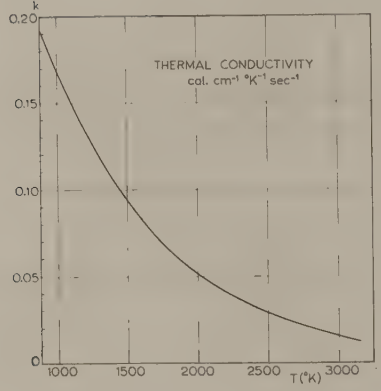

Fig. 8.

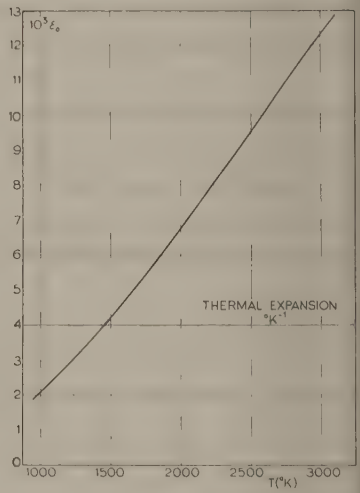

Fig. 9.

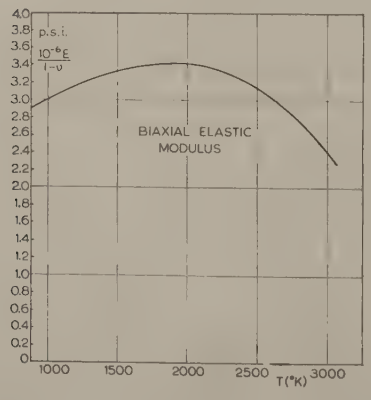

Fig. 10.

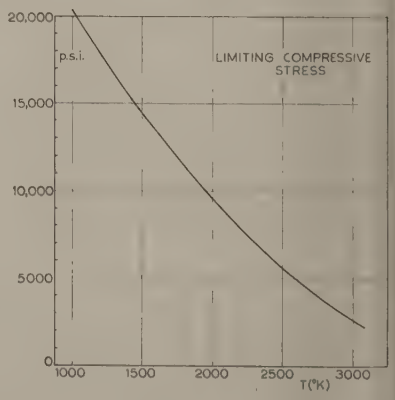

Fig. 11.

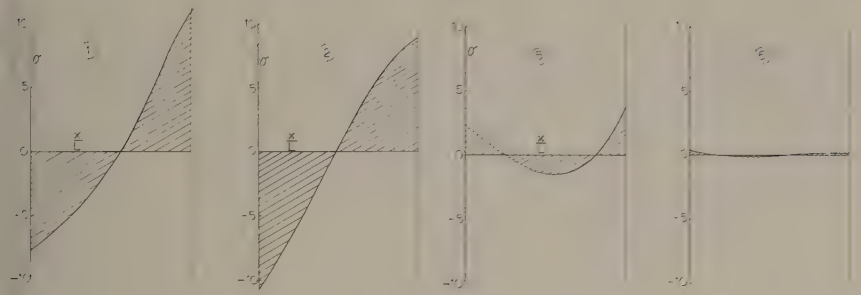

Fig. 12.

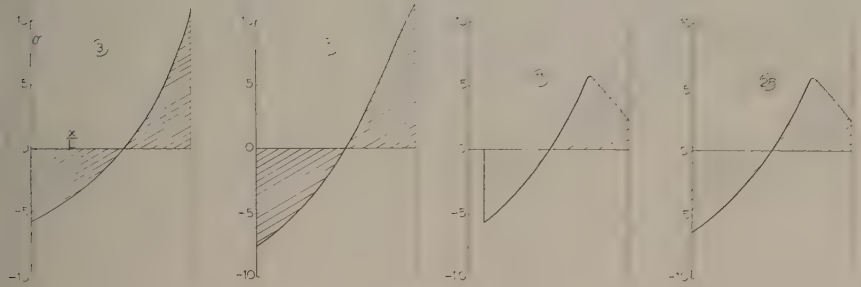

Fig. 13.

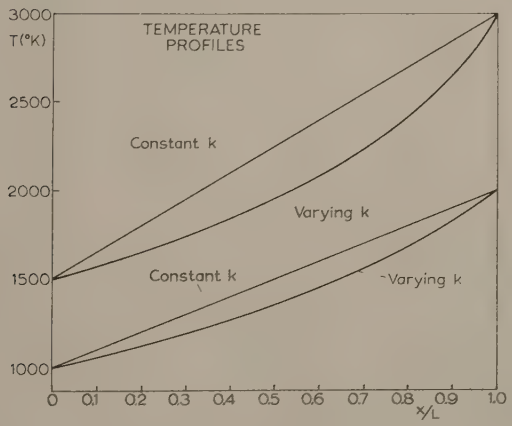

Fig. 14.

In Fig. 12, curve (1) is the stress profile calculated for k, α, E' varying with temperature as shown but with no compressive stress limit *i.e.* no "ductility". The plate is not allowed to bend. If bending is allowed the curve (5) results. Curves (2) and (6) are the corresponding curves for constant thermal conductivity. It can be seen that the stresses for a plate which is free to bend are sensitive to the variation of conductivity The simple theory predicts zero stress for case (6). That the stresses in curve (6) are not quite zero must be ascribed to the slightly non-linear expansion curve. The stress units are thousands of pounds per square inch.

Fig. 13 shows results in which curve (1) is the same as before, for comparison, whereas for curve (3) constant elastic modulus, the same at all temperatures, was used. Curves (11) and (28) show the result of including the compressive stress limit while in (11) the tensile stress has been assumed zero for any strain greater than 0.2%.

With regard to possible application of this method to metals we should say that creep and work-hardening have not yet been considered, but were it sufficiently worth while we see no fundamental obstacle to programming for their effects. The difficulty would seem to lie in finding a field in which (a) the fundamental material properties are well enough known as functions of temperature and (b) experimental evidence might be forthcoming to check the theory.

THE HIGH TEMPERATURE STABILITY OF OXIDES AND SULPHIDES

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I. GENERAL STABILITY OF OXIDES

The metal oxides include some of the most stable chemical compounds known and many have very high melting points. The high stability of some oxides is shown in Fig. 1 where the free energy of formation of the oxides ($-\Delta G°$,298°K), taken from COUGHLIN[1], is plotted against the atomic number of the elements in the periodic table; where several oxides are formed, the value for the most stable only is plotted. In the horizontal series of elements through groups I to VIII in the periodic table, a maximum occurs in thermodynamic stability; in the earlier part of the table this is associated with the alkaline earth oxides BeO, MgO, CaO and SrO. Barium oxide also has a large free energy of formation but there is a further rise in thermodynamic stability in the oxides of the rare earths, although values for some of these are not known. The oxides of the actinide group metals are also very stable.

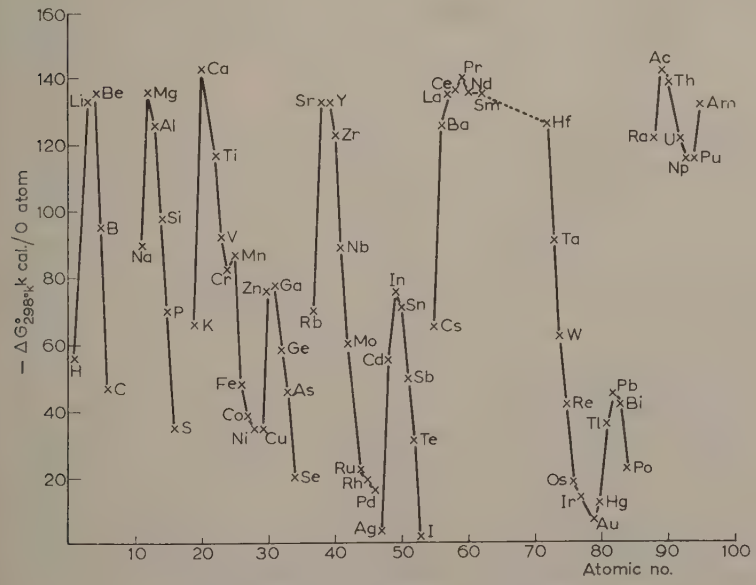

Fig. 1. Thermodynamic stability of the oxides.

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From the point of view of low reactivity at high temperatures those oxides with a free energy of formation less than 100 kcal/g.atom oxygen have little value; in Table I, those both of high melting point and high thermodynamic stability are listed.

TABLE I

FREE ENERGY OF FORMATION, MELTING POINT AND VAPOUR PRESSURE OF REFRACTORY OXIDES

Oxide	$-\Delta G°$, 298°K (kcal/g.atom O)	*Melting point* (°K)	*Vapour pressure*, 2000°K (atm.)
CaO	143.3	2873	2.5×10^{-7}
Ac_2O_3	141.7		
ThO_2	139.6	3573	
Pr_2O_3	140.2		
Ce_2O_3	137.2		
Sm_2O_3	136.8		
Nd_2O_3	136.3		
BeO	136.1	2823	4.9×10^{-8}
MgO	136.1	3073	7.2×10^{-4}
La_2O_3	135.6	2638	
SrO	134.0	2688	5.8×10^{-6}
Am_2O_3	135.7		
Y_2O_3	132.7	2683	
BaO	126.5	2190	1.1×10^{-4}
HfO_2	125.9	3083	
Al_2O_3	125.8	2313	5.7×10^{-6}
ZrO_2	123.9	2950	10^{-6}
UO_2	123.3	3148	9.0×10^{-8}
RaO	123.0		
PuO_2	116.8		
NpO_2	116.8		
TiO_2	106.2	2113	
CeO_2	115.0	2873	

Calcium oxide is the most stable of all at 298°K but has been restricted in use because of its tendency to hydrate; it also is easily reduced above the boiling point of calcium and a considerable vapour pressure makes operation in vacuo above 2000°K impracticable. Nothing is known of the behaviour of Ac_2O_3 but ThO_2, the next in order of stability, is one of the most useful oxides. It is unchanged in oxidising atmospheres up to the melting point and is non-volatile in vacuo up to 2300°K. In reducing conditions it can not be regarded as unreactive at moderate temperatures due to the possible formation of ThO which is closely similar in thermodynamic stability to ThO_2.

The rare earth oxides Pr_2O_3, Ce_2O_3, Sm_2O_3 and Nd_2O_3 have been little studied but they should show strong similarity to La_2O_3 which has promising behaviour in vacuo and oxidising conditions. Beryllia is probably the only oxide which is equally of use in oxidising, reducing and vacuum conditions, forming no higher or lower oxide and being non-volatile in vacuo up to 2273°K. Due to the highly toxic nature of beryllium[2] however, its use had been very restricted although favourable nuclear properties has renewed interest in its development. In use, moist atmospheres must be avoided at high temperatures because of the formation of a stable gaseous compound, possibly $Be(OH)_2$ (g), in appreciable quantity above 1200°–1400°C.

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Magnesia has value in oxidising conditions but in reducing atmospheres it is easily reduced and, in vacuo, is highly volatile above the boiling point of magnesium (1370°K). Little information is available on Y_2O_3 but on general grounds it should be valuable in oxidising or vacuum conditions. Knowledge of HfO_2 is limited and the difficulties of separation from ZrO_2 have restricted a study of its behaviour. It is unlikely to behave very differently from ZrO_2 but is probably somewhat better in performance. Zirconia is a most useful oxide in oxidising or vacuum conditions, provided it has been stabilised against allotropic transformation from the tetragonal to monoclinic form, a qualification which would also apply to HfO_2.

Alumina is the most common refractory oxide and is probably the only one easily obtained in impermeable form at the present time. Its principal value is in oxidising conditions up to 2073°K; in reducing atmospheres reaction is extensive and in vacuo volatility is appreciable. Urania is a stable oxide in vacuo or reducing atmospheres up to 2273°K but in oxidising atmospheres will form higher oxides. Plutonium dioxide has a lower melting point than UO_2 and may be useful in oxidising atmospheres as no oxide higher than PuO_2 appears to be stable. In reducing conditions Pu_2O_3 would probably form and in vacuo volatility may be considerable.

No information is available on NpO_2, and TiO_2 has little value as a refractory as the melting point is comparatively low and reduction to a lower oxide readily occurs. Ceria is easily reduced by hydrogen to Ce_2O_3 but has some application in oxidising atmospheres.

In assessing the suitability of a material for use at high temperatures it is necessary to consider the free energy of formation at the temperature of interest and not at 298°K as the stability of oxides decreases with increase in temperature, as shown in Fig. 2 for BeO, HfO_2 and MgO. With MgO there is the additional factor that magnesium has a low boiling point and above that temperature, the stability of the oxide is correspondingly reduced.

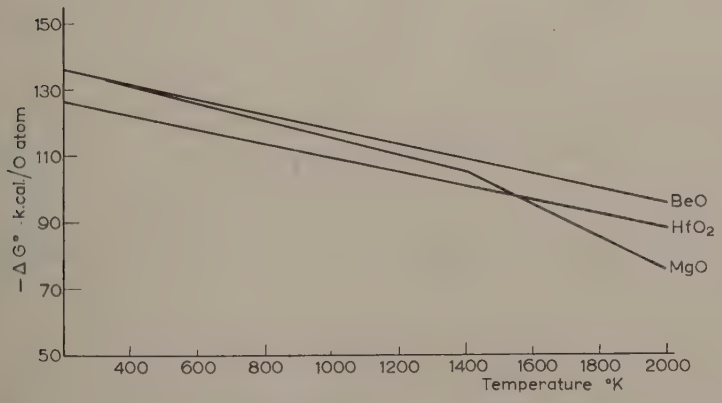

Fig. 2. Variation of free energy of formation with temperature for BeO, MgO, HfO_2.

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In vacuo, the use of many oxides is restricted because the volatility is high. Several modes of vapourisation are possible as in the following example for an MO_2 oxide:

$$MO_2(s) \rightleftharpoons M(g) + O_2(g) \quad (1)$$

$$MO_2(s) \rightleftharpoons MO_2(g) \quad (2)$$

$$MO_2(s) \rightleftharpoons MO(g) + {}^1/_2O_2(g) \quad (3)$$

$$2MO_2(s) \rightleftharpoons M_2O_4(g) \quad (4)$$

This does not exhaust all possible mechanisms but where a process similar to (2), (3) or (4) occurs then the measured vapour pressure is higher than the decomposition pressure calculated from the thermodynamics relating to equation (1). By comparing the measured pressure with the calculated decomposition pressure it can be established if molecular vapourisation is taking place, but to determine which molecular species are present, mass spectrographic methods must be employed.

In Table II the measured vapour pressures of some oxides are compared with the decomposition pressure at 2000°K.

TABLE II

VAPOUR PRESSURES AND DECOMPOSITION PRESSURES OF OXIDES

Oxide	*Vapour pressure, 2000°K (atm.)*	*Decomposition pressure, 2000°K (atm.)*
CaO	2.5×10^{-7} (7)	2.1×10^{-7}
ThO_2		1.8×10^{-15}
BeO	8.3×10^{-9} (8)	6.6×10^{-9}
MgO	7.2×10^{-4} (9)	5.0×10^{-6}
La_2O_3		4.3×10^{-12}
SrO	5.8×10^{-6} (10)	6.9×10^{-7}
Y_2O_3		1.6×10^{-11}
HfO_2		1.0×10^{-15}
BaO	1.1×10^{-4} (11)	1.0×10^{-6}
Al_2O_3	5.7×10^{-6} (12)	2.6×10^{-8}
ZrO_2	10^{-6} (4)	3.3×10^{-14}
UO_2	9.1×10^{-8} (13)	4.6×10^{-13}
TiO_2		1.5×10^{-10}
CeO_2		2.3×10^{-9}

Of those shown, only BeO, MgO and CaO are known to vapourise to the elements at least under neutral or reducing conditions and although the vapour pressures quoted in Table II for MgO indicates molecular vapourisation, other evidence rather indicates decomposition[4,5]. There is some uncertainty about the mechanism for SrO[4,5], but the other oxides have vapour pressures appreciably greater than the decomposition pressure. Some of the gaseous molecules which have been observed are ThO(g), ThO_2(g), LaO(g), HfO(g), HfO_2(g), BaO(g), Al_2O(g), ZrO(g), ZrO_2(g), UO_2(g), and TiO(g)[5].

II. GENERAL STABILITY OF SULPHIDES

The properties of a number of refractory sulphides are shown in Table III together with the heat of formation of the corresponding oxide.

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TABLE III

MELTING POINT AND HEAT OF FORMATION OF SULPHIDES, AND HEAT OF FORMATION OF CORRESPONDING OXIDE

Sulphide	*Melting point* (°K)	$-\Delta H°,298°K$ (kcal/g.atom S)	$-\Delta H°,298°K$ (kcal/g.atom O)
BaS	>2470	126.7	133.5
BeS	—	71.0	143.1
CaS	—	128.9	150.7
CeS	2725	126.9	
Ce_3S_4	2325	116	
La_2S_3	2273	114	142.8
MgS	>2270	99.9	143.8
Nd_2S_3	2473	114	
SrS	>2270	128.6	141.1
ThS	2500	120	
Th_2S_3	~2300	102	
ThS_2	2203	85	
TiS	2273	—	

n general the free energy of formation is smaller than for the oxides, although the ulphides of Ca, Sr and Ba closely approach the oxides in stability. In oxidising at-nospheres, they react readily to form the oxide and their principal attraction is the)ossibility of operation in vacuo or inert atmospheres for the containment of liquid netals. The volatility is appreciable but ThS can be used to 2500°K, the others be-oming of greater possible use as the temperature is lowered or vacuum is replaced)y inert gas. BREWER[14] listed the volatilities of sulphides as shown below, non-volatile)eing taken to mean a vapour pressure less than 10^{-7} atm., moderately volatile 10^{-6}–10^{-7} atm. and readily volatile greater than 10^{-6} atm.

500°K: ThS moderately volatile; US and CeS rapidly volatile.

000°K: ThS, Th_2S_3, Th_4S_7 and US non-volatile; CeS and Ce_3S_4 slowly volatile; BaS rapidly volatile.

500°K: ThS, Th_2S_3, Th_4S_7, US, CeS, Ce_3S_4, Hf_2S_3, Zr_2S_3 and BaS non-volatile; other rare earth sulphides and the sulphides of Nb, Y and Sc included.

The sulphides of thorium, uranium, barium and cerium have been used with some uccess for melting liquid metals[15 18]. Barium sulphide was found suitable for use vith metals up to 1873°K and CeS for melting most metals with melting points less han 2073°C. Thus U, Ce, Th, Mg, Be, Bi, Al, Fe, Ti, Sn and Zn have been melted with ittle sulphur pick up. Thorium sulphide behaves similarly to CeS and is somewhat)etter under the most severe conditions; for example U can be heated to 2173°K in 'hS and still be removed easily from the crucible when cold, indicating little reaction. 'he degree of contamination with S from these sulphide crucibles has not been in-'estigated closely but the general behaviour towards reactive liquid metals is cer-ainly promising compared to other refractory materials. Generally speaking if the netal being contained forms a sulphide which enters into solid solution with the rucible, then attack is minimised; if a highly volatile substance forms then the degree)f attack is much greater.

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III. REACTION WITH METALS

The standard free energy change (ΔG°) for the reaction of metal–oxide and metal–sulphide systems has large positive values in many cases, indicating that no reaction will take place. In practice, some reaction is always observed and contamination of the metal results. This apparent conflict between thermodynamic prediction and actual experiment exists because the standard free energy change refers to reactants and products in a state of unit activity (pure solid, pure liquid, gas at 1 atm.) but in practice the products, either because they are gaseous or can exist in solution in one or other of the reactants, may be formed with activities less than the equilibrium values; reaction then takes place with a decrease in free energy of the system until equilibrium is reached. For given values of activity in a reaction

$$A + B \rightleftharpoons C + D \tag{5}$$

the actual free energy change is given by

$$\Delta G_T = \Delta G^\circ_T + RT \ln \frac{Q_C Q_D}{Q_A Q_B} \tag{6}$$

where Q_A etc. are the respective activities. Little is known of the activities of oxygen and sulphur in various metals so the degree of contamination of a metal in most metal oxide or metal–sulphide systems can only be obtained by experiment. In addition where a product is gaseous and is continuously removed, the system never reaches equilibrium and the reaction proceeds completely. The standard free energy change is therefore only an indication of the maximum degree of reaction, if equilibrium is attained; the more positive the value, the smaller the degree of reaction. But even in such a case, alternative reactions are possible, other than that to which a particular ΔG° applies, and experimental investigation is still necessary.

A number of possible ways in which ceramic and metal phases can interact are shown in the following examples on oxides.

(a) Between liquid aluminium and MgO at 1400°K, a possible reaction could be

$$MgO_{(s)} + {}^2/_3\, Al_{(l)} \rightleftharpoons Mg_{(g)} + {}^1/_3\, Al_2O_{3(s)} \tag{7}$$

for which the standard free energy change $\Delta G^\circ = 1.85$ kcal. The equilibrium constant $K_p = p_{Mg(g)}$, taking all other phases to have unit activity, and since

$$\Delta G^\circ = -RT \ln K_p \tag{8}$$

the equilibrium partial pressure $p_{Mg(g)} = 0.5$ atm. In flowing gas or in vacuo, this represents very rapid loss of $Mg_{(g)}$ and containment of the liquid metal is unsatisfactory.

(b) Containment of a liquid metal such as titanium is also unsatisfactory; in addition to the formation of $Mg_{(g)}$, titanium has a high solubility for oxygen and the following phases co-exist:

$$MgO_{(s)} \rightleftharpoons Mg_{(g)} + O_{(Ti)} \tag{9}$$

As this reaction proceeds due to removal of $Mg_{(g)}$ the phases $TiO_{(s)}$ and $TiO_{2(s)}$ may ultimately form.

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c) Liquid silicon in alumina at 2000°K may involve the following reaction

$$^1/_2\,Al_2O_{3(s)} + Si_{(l)} \rightleftharpoons {}^1/_2\,Al_2O_{(g)} + SiO_{(g)} \qquad (10)$$

or which the standard free energy change $\Delta G^\circ_{2000^\circ K} = 27.5$ kcal. The equilibrium ressure $p = p_{Al2O(g)} + p_{SiO(g)} = 0.018$ atm. This is appreciable and in vacuo ould represent extensive reaction between these phases by this particular mechanism.

d) Liquid uranium in ThO_2 could undergo the following reaction

$$ThO_{2(s)} + U_{(l)} \rightleftharpoons UO_{2(ThO2)} + Th_{(s)} \qquad (11)$$

lthough the standard free energy change is positive. In this type of reaction, as there s no gaseous phase, the extent of reaction is limited by the position of equilibrium.

In some cases, although reaction initially occurs, further reaction is restricted y the formation of an interfacial product; for example, forsterite ($2\,MgO{\cdot}SiO_2$) forms etween silicon and MgO and a $BeO-Al_2O_3$ compound, probably chrysoberyl ($BeO{\cdot}l_2O_3$) forms between beryllium and Al_2O_3[19]. In all systems, some reaction is unvoidable and rates at high temperatures are unlikely to be slow enough to help ppreciably in restricting it. However, other methods to minimise reaction could be ied as discussed by BREWER[20] for example in the choice of a container for melting tanium. It is suggested that before fabrication, the refractory material is saturated ith titanium at the temperature of interest. Provided this does not drastically lower ıe melting point, the only possible reaction during experiment would be solution the container in the liquid metal and under certain conditions, the rate and extent this may be quite small.

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ATMOSPHERIC CONTAMINATION OF CHROMIUM AND ITS EFFECT ON MECHANICAL PROPERTIES

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(Received November 25th, 1958)

SUMMARY

Chromium heated in air at 950°C for 200 hours is contaminated to a considerable extent by nitrogen. This has a marked effect on the mechanical properties, especially the ductile → brittle transition temperature, the magnitude of the effect depending on the rate of cooling from 950°C.

INTRODUCTION

One of the problems in developing chromium-base alloys for use in aircraft gas turbine engines is that of brittleness at ordinary temperatures. It has now been established that the behaviour of chromium is influenced by purity, particularly nitrogen content, by surface condition, and by metallurgical structure[1,2]; progress is also being made in achieving room temperature ductility on chromium alloys[3]. Since these materials will have to operate in service, however, for prolonged periods at temperatures of at least 950°C in atmospheres containing nitrogen and oxygen, it is important to know how much contamination does occur, and whether this contamination has a significant effect on mechanical properties, in particular, the ductile → brittle transition temperature.

Although chromium itself is not likely to be used in gas turbine engines, it is necessary to first establish the behaviour of the basis metal, so that the influence of alloy additions on atmospheric contamination and its effects can subsequently be determined for practical chromium-base alloys.

EXPERIMENTAL PROCEDURE AND RESULTS

Material

Electrolytic chromium, containing 0.0005–0.001% nitrogen, 0.01–0.02% oxygen, and total metallics < 0.01 wt.-%, was arc melted to give ingots 1 1/2 in. diameter by 4 in. long. For preparation of mechanical test pieces, ingots were extruded to 1/2 in. diameter bar, care being taken at all stages to avoid pickup of impurities.

Extent of atmospheric contamination

Atmospheric contamination was investigated using ingots rather than mechanical test pieces, so that sufficient sample at various depths could be obtained for chemical analysis. The ingots were heated in air at 950°C for 200 h in an electric resistance fur-

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ace, the size of which was large in relation to the ingots. Samples for chemical ana-ysis were obtained by turning along the length of the ingot; this was done under a tream of alcohol as described elsewhere[4], to avoid pickup of impurities.

Nitrogen was determined by the micro-Kjeldahl method and oxygen by vacuum asion. There was substantial penetration by nitrogen as shown in Fig. 1; nitrogen as penetrated to a depth of 1/4 in. On the other hand, no penetration by oxygen was etected. Microscopic examination showed both a chromium nitride and a chromium xide layer at the surface, similar to that shown in Fig. 2, the nitride being under he oxide. The thickness of the oxide layer was 0.001 in., but the nitride layer varied onsiderably, ranging from 0.0001 to 0.0005 in. in depth.

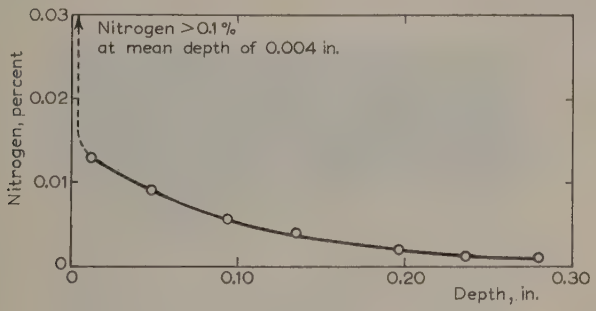

Fig. 1. Penetration of nitrogen in chromium ingot after heating in air at 950°C for 200 h.

ig. 2. Oxide and nitride layers at surface of chromium tensile specimen after heating in air at 950°C for 200 h (×250).

ffect of atmospheric contamination on mechanical properties

Tensile specimens, with a gauge length of 1 in., and gauge diameter of 0.210 in. ith two diametrically opposite flats 0.1 in. apart along the gauge length, were ma-ined from the extruded bars. The extruded stock was essentially in the strain-free ondition, with an average grain size of 0.05 mm; the transition temperature of this

eferences p. 156

material was above room temperature (see A in Table I). Although it would have been preferable to use chromium which was initially ductile at room temperature, changes in properties due to changes in metallurgical structure during the heating would have occurred, leading to complications of the present issue.

The test specimens were electropolished to remove surface distortion and imperfections produced by the machining. They were then heated in air at 950°C for 200 h, in the same way as for the ingots previously considered. Microscopic examination again revealed both an oxide and nitride layer at the surface (Fig. 2). The oxide layer appeared to be of the same thickness as that on the ingots. The average thickness of the nitride layer, however, was more than on the ingots, and the apparent variation in depth was greater, ranging from 0 to 0.002 in. An extreme example of this variation in depth is given in Fig. 3, showing a substantial nitride layer completely fading out

Fig. 3. Same specimen as in Fig. 2, showing fade-out of nitride layer at surface (×250).

Fig. 4. Coarse precipitate of chromium nitride in chromium tensile specimen after heating in air at 950°C for 200 h followed by furnace cooling (×750).

at the surface. The reason for the variation in this nitriding behaviour is not at present understood. The average nitrogen content was 0.08 wt.-%, and with the nitride layer removed it was 0.011 wt.-%. These results suggest that the nitrogen gradient would be similar to that of the ingot (Fig. 1), but since the minimum distance to the specimen

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axis was only 0.05 in., the nitrogen content at the centre of the test specimens must still be about nine times the original basis figure of 0.001 wt.-%. Nitride precipitates were observed in the interior of these specimens situated both within the grains and at the grain boundaries as shown in Fig. 4. However, the size and distribution of these precipitates depended on the rate of cooling from 950°C; the slower the cooling rate the greater their size and the greater the amount at the grain boundaries.

The mechanical tests were carried out in a tensile machine specially designed for straining at constant rates over a wide range of strain rates. A typical set of results for a crosshead travel rate of 6×10^{-2} in./min is given in Table I. This shows that atmospheric contamination had a significant effect on the ductile → brittle transition temperature. Firstly, the transition temperature was dependent on the rate of cooling from 950°C; the slower the cooling rate the lower the transition temperature, so that for relatively slow rates of cooling (see B(1) and B(2) in Table I) the transition temperature was considerably below that of the as-extruded material. Only for very fast cooling rates did the transition temperature exceed that of the reference material. Secondly, the transition from the fully ductile to the completely brittle condition occurred over a relatively wide range of temperature, as distinct from the rather abrupt change shown by material in the as-extruded condition. This feature was more apparent for the slower and faster rates of cooling (see B(1) and B(3) in Table I). In addition to

TABLE I

COMPARISON OF MECHANICAL PROPERTIES OF CHROMIUM IN THE AS-EXTRUDED CONDITION WITH EXTRUDED CHROMIUM HEATED IN AIR AT 950°C FOR 200 HOURS AND COOLED AT DIFFERENT RATES

Condition	*Temperature of test, °C*	*Elongation to fracture, %*	*Yield stress, tons sq. in.*	*Maximum nominal stress, tons/sq. in.*
A. As-extruded	225	0	—	15.8
	250	37.2	9.5	16.0
	400	32.0	12.6	15.5
	500	36.0	7.0*	14.4
B. Heated in air at 950°C for 200 h	20	0	—	10.3
(1) Furnace cooled	50	0.2+	10.7*	10.9
	100	3.1+	5.7*	11.1
	150	35.5+	4.2*	15.8
	200	48.8+	7.3*	15.7
(2) Cooled in stream of helium	150	0	—	10.1
	175	1.2+	7.3*	9.5
	200	36.5+	9.0*	15.9
(3) Water quenched	350	0	—	17.7
	375	0.4+	14.2*	16.1
	400	0.8+	13.3*	18.0
	450	4.7+	9.5**	20.1
	500	24.2+	8.1**	16.5
	550	29.6+	4.8*	14.1

+ Measured between shoulders of specimens ($1\frac{1}{4}$ in.); not possible to inscribe 1 in. gauge marks due to hard nitride layer.
* No drop in stress.
** Small drop in stress (multiple yielding).

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changes of transition temperature, there were also changes in yielding behaviour. Plastic deformation occurred without any drop in stress in the majority of the contaminated specimens; at the most there was merely an arrest in the tensile curve, whereas the as-extruded material invariably showed marked yield points, at least in the ductiln range below 450°C. Only water quenched specimens strained at 450–500°C showed any indication of yield points; in this case, multiple yielding occurred, but the drop ie stress at any point was extremely small. Heating alone (*i.e.* by heating in vacuo at 950°C for 200 h and then cooling at different rates) had no significant effect on the mechanical properties. Of considerable interest was the fact that the oxide and nitride surface layers on contaminated specimens always behaved in a completely brittle manner in the mechanical tests.

The same general results were obtained for much slower strain rates, except that the transition temperature of all specimens tended to be lower (*e.g.* at a crosshead travel rate of 10^{-3} in./min there was some evidence of ductility at room temperature (20°C) for the contaminated specimens furnace cooled from 950°C).

CONCLUSIONS

(1) Chromium heated in air at 950°C for 200 h is contaminated to a considerable extent by nitrogen.

(2) The mechanical properties of such material are dependent on the rate of cooling from 950°C. Despite the presence of a brittle oxide and nitride skin at the surface, the ductile→brittle transition temperature is substantially lower than in the as-extruded material for slow rates of cooling. Even for very rapid rates of cooling, chromium is fully ductile at temperatures well below the proposed operating range. Moreover, the transition zone from fully ductile to completely brittle behaviour is extended over an appreciable temperature range. Changes are also produced in the yielding behaviour, in that yield points are absent over the temperature range where there are marked yield points in the as-extruded material.

(3) The amount of coarse chromium nitride precipitate observed in the interior of contaminated chromium increases as the rate of cooling from 950°C decreases; this is in the direction of lowering the transition temperature. Accordingly, the amount of nitrogen remaining in solution and/or as a fine precipitate and causing embrittlement, becomes less and less as the rate of cooling is decreased.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. J. I. NISH for his helpful advice and encouragement, and Mr. J. D. EYRE for assisting with the mechanical tests. The paper is published by permission of the Chief Scientist, Australian Defence Scientific Service, Department of Supply, Melbourne, Australia.

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THE EQUILIBRIUM DIAGRAM OF THE SYSTEM BISMUTH–PALLADIUM

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The Department of Metallurgy, The University Museum, Oxford (Great Britain)

(Received December 23rd, 1958)

SUMMARY

The equilibrium diagram of the system bismuth–palladium has been studied in the region 0–65 at.-% Pd by thermal analysis and microscopical methods. The freezing point of bismuth is depressed by the addition of palladium and sinks to a eutectic at 5.83 at.-% Pd and 256°C. The liquidus then rises to 485.4°C, at which temperature the compound "Bi_2Pd" melts without change of composition. The compound BiPd gives rise to a pronounced maximum in the liquidus curve at 618°C, and there is a palladium-rich eutectic at 577°C. At low temperatures the composition of the "Bi_2Pd" phase is about 34 at.-% Pd. It undergoes a transformation at 380°C, in contrast to the earlier work of ZHURAVLEV AND ZHDANOV, according to whom the transformation took place at 200°C. There is a remarkable resemblance between the equilibrium diagrams of the systems Pd–Sb and Pd–Bi. Both give rise to compounds of the type PdX_2, the melting points of the Sb-compounds being systematically higher.

INTRODUCTION

The use of liquid bismuth as a solvent for uranium in nuclear metallurgy has led to interest in the equilibrium diagrams of the alloys of bismuth with the metallic elements produced as fission products. These include the group ruthenium, rhodium and palladium, and the present paper describes an investigation of the constitution of bismuth-rich alloys of the system Bi-Pd*.

At the beginning of the present work, a preliminary equilibrium diagram had been published (without experimental details) by ZHURAVLEV AND ZHDANOV[1], according to which the system (Fig. 1) contains compounds BiPd and Bi_2Pd. HEYCOCK AND NEVILLE[2] had measured the depression of freezing point of bismuth, but otherwise there appeared to be no accurate work on the equilibrium diagram, although the compounds have been studied because they exhibit supraconductivity.

EXPERIMENTAL DETAILS

(1) *Materials used*

The bismuth used in the present work was special high purity metal kindly presented by the Atomic Energy Research Establishment, Harwell.

The palladium was added in the form of master alloys prepared from metals of high purity by Messrs. Johnson, Matthey & Co., Limited. One master alloy contained 4.3% Pd*, and on exposure to air became gradually coated with a mauve tarnish

* Chemical symbols are used for abbreviation, and all compositions are in atomic percentages.

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which could be removed with dilute nitric acid. The second master alloy containing 51.7% Pd remained untarnished.

(b) Cooling curve methods

The alloys of lower melting point were melted in graphite crucibles provided with lids of graphite through which holes were drilled to admit the silica stirrer and thermocouple sheath. These were heated in a nichrome-wound resistance furnace, and after thorough stirring of the melt, the current was adjusted to give a cooling rate of the order 2–3°/min at the expected liquidus point, and the cooling curve was taken with continual stirring of the melt. All the standard precautions necessary to obtain high accuracy[3] were taken. The thermocouples were recalibrated regularly, and the constancy of the measured values of the eutectic horizontals provided a further check on the accuracy of the pyrometry.

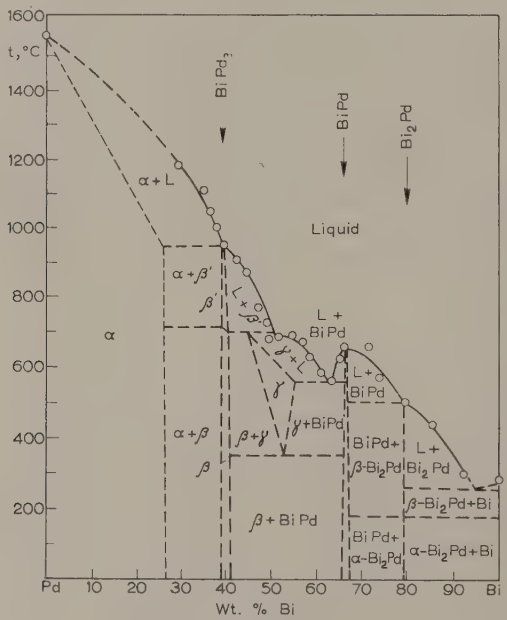

Fig. 1. From Russian source.

For the alloys of higher melting point, the cooling curves were taken in an atmosphere of argon in a closed tube apparatus similar to that of HELLAWELL AND HUME-ROTHERY[4] whose general experimental methods were followed. The crucibles and thermocouple sheaths were of pure alumina.

(c) Preparation and heat-treatment of solid alloys

Alloys containing less than 2% Pd were melted in closed graphite crucibles, and were cast into graphite moulds 2 inches long and 1/4-inch diameter. For alloys of higher

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Pd content, melting was carried out under a low melting flux before casting into graphite moulds. The flux consisted of 320 parts of potassium chloride, 60 parts of sodium chloride, 40 parts of calcium fluoride, and 896 parts of anhydrous magnesium chloride. The resulting ingots were sound, and of uniform composition. Some specimens of the equiatomic alloy were also prepared in sealed evacuated silica tubes. The alloy was heated until molten, thoroughly shaken, and the whole then quenched into cold water.

The specimens were annealed in sealed evacuated tubes of hard glass or silica, heated in electric resistance furnaces whose temperatures were controlled to within ± 1°C by expansion controllers. After quenching into iced water, the specimens were prepared for microscopical examination by conventional methods; the best results were obtained by hand polishing using γ-polishing alumina on a selvyt cloth. In most cases the microstructures were revealed clearly in the polished and unetched specimen but, where etching was required, satisfactory results were obtained with (a) dilute alcoholic nitric acid, (b) dilute aqueous nitric acid, or (c) a dilute aqueous solution of chromic and sulphuric acids.

(d) Separation of phases by acid-extraction

As explained below, it was sometimes necessary to extract crystals from alloys which had been quenched from the two-phase (liquid + solid) state. For this purpose the alloy was heated to 100°C above its liquidus point with thorough stirring, and was then cooled slowly to the desired temperature at which it was maintained for 24 hours before the ingot was quenched into iced brine. After breaking into fragments, the alloy was placed in a porcelain crucible and covered with water, to which concentrated nitric acid was slowly added until the solution was just strong enough for the bismuth-rich eutectic constituent to be attacked. The residual crystals were washed with water and alcohol, and dried in a current of warm air.

(e) Analysis of alloys

Cooling curve ingots were split longitudinally, and one half was dissolved for analysis, the other half being retained for microscopical examination.

EXPERIMENTAL RESULTS

(a) The liquidus curve

The primary (liquidus) arrests from the cooling curves are summarised in Table I, and are plotted in Fig. 2.

The addition of palladium to bismuth results in a depression of the liquidus curve which falls to a eutectic point at 5.8% Pd and 256.0°C. The constituents of the eutectic are almost pure bismuth, and an intermediate phase (p. 162) containing 34% Pd, this composition corresponding almost to the formula Bi_2Pd. The present results are in good agreement with those of HEYCOCK AND NEVILLE[2] if the latter are raised by 2°C to allow for the fact that their value for the freezing point of bismuth was 2°C lower than the present accepted value.

With increasing Pd-content the liquidus rises to 380°C, at which temperature the 'Bi_2Pd" phase appears to undergo a polymorphic transformation. On heating curves, the arrests corresponding to this transformation varied from 377.2 to 384.0°C in diffe-

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rent experiments, but on cooling curves the arrests showed supercooling and recalescence and were from 10 to 12 C lower. The mean value of the heating curve arrests is preferred. The mean value of the heating curve arrests for alloys containing less than 33.3% Pd was slightly lower than that for alloys of higher Pd content. This suggests

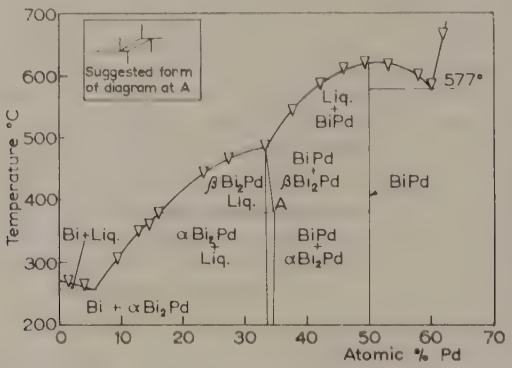

Fig. 2. For reasons of clarity, some of the liquidus points for bismuth-rich alloys have been omitted.

that the equilibrium diagram is of the form shown in Fig. 2, but the evidence is not conclusive.

With further increase in the Pd-content, the liquidus curve rises until, at 485 C and 33.3% Pd, the Bi_2Pd phase melts without change of composition, but without a maximum in the liquidus (Fig. 2). The liquidus curve continues to rise to a well marked maximum at 620°C and approximately 50% Pd, and then sinks to a second eutectic point at 677°C and 60% Pd.

(*b*) *The solid solubility of palladium in bismuth*

Alloys containing approximately 1.0, 0.5, 0.3, and 0.1% Pd were annealed at 245° C for 5 days and quenched. All were found to be two-phase and the 0.1% alloy remained two-phase after annealing for a further 5 days. The solubility of Pd in bismuth is therefore very small.

(*c*) *The structure of the Bi/Bi_2Pd eutectic*

The Bi/Bi_2Pd eutectic is remarkable for the great variation in the scale of the two-phase pattern. Fig. 3 shows the structure (× 200) of an alloy of almost exactly the eutectic composition and this shows two patches whose structure is almost too fine to be resolved at a magnification of 200, together with a large area of much more coarse material. This characteristic is maintained in both hypo- and hyper-eutectic alloys provided that the eutectic is present in large quantities.

(*d*) *The composition of the "Bi_2Pd" phase*

The low temperature "Bi_2Pd" phase forms long needle-shaped crystals. These

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TABLE I

Composition of alloy (at.-% Pd)	*Liquidus point (°C)*
0	270.6
1.01	268.0
1.54	266.4
4.05	260.5
5.8*	256.0*
5.83	256.2
9.00	300.2
12.61	348.8
15.24	360.2
16.01	377.3
16.4 (e)	380 (e)
23.23	442.3
27.34	466.2
33.27	485.0 (f)
37.53	541.2
42.06	585.5
46.00	612.0
49.52	618.0
53.15	615.2
57.93	602.5
60 (s)	577.0
61.86	657.8

* The value 256.0°C was obtained in 13 separate cooling curve experiments. The composition 5.8 is obtained by extrapolation of the preceding liquidus points to meet the eutectic horizontal.

(e) This composition is obtained by extrapolation of the liquidus points to meet the horizontal at 380°C.

(f) This alloy appears to be very slightly on the Bi-rich side of the "Bi_2Pd" horizontal in the diagram, the mean temperature of which from heating and cooling curve arrests was 485.4°C.

(s) Synthetic composition.

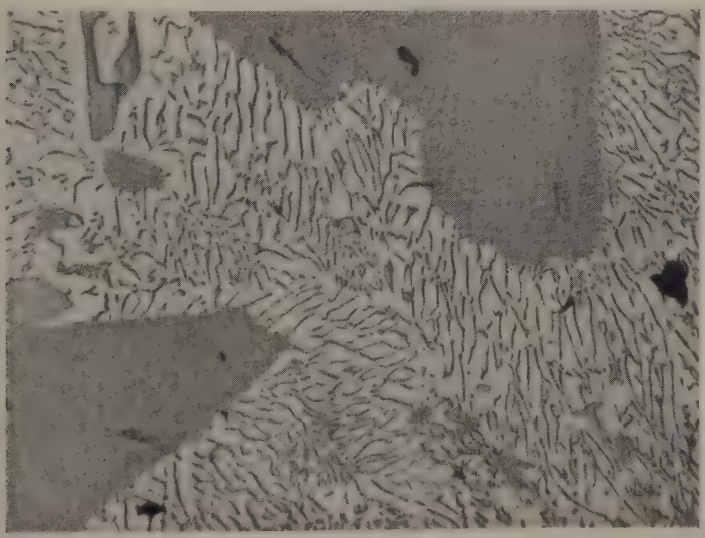

Fig. 3. Bi/Bi_2Pd eutectic (× 200).

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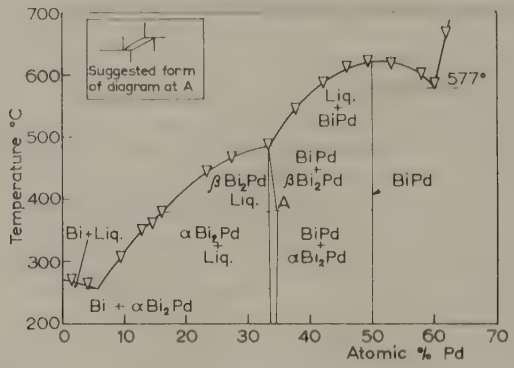

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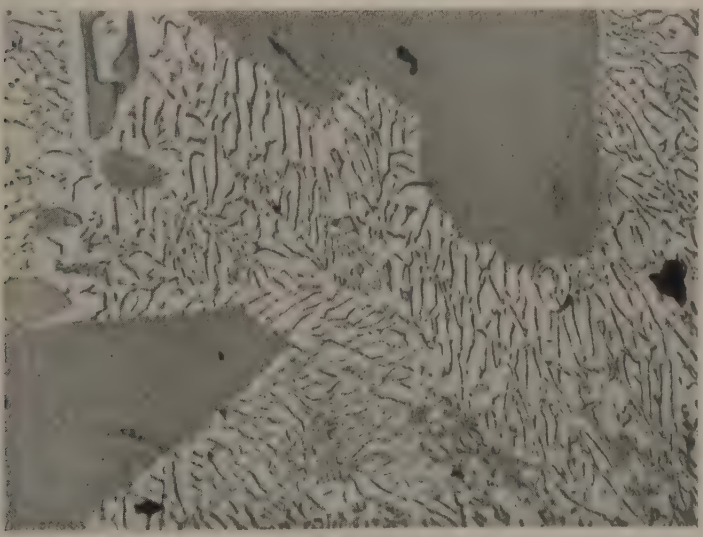

Fig. 3. Bi/Bi_2Pd eutectic (× 200).

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were readily apparent in the microstructures, and many were sufficiently long to be picked out by tweezers from the extraction residues. Crystals extracted from an alloy annealed in the two-phase (solid + liquid) region at 265°C contained 34.31% Pd by analysis. The danger of this experimental method is that Bi-rich chilled liquid may be included in the crystals, giving too low an apparent content of Pd by analysis.

In a series of chill castings annealed for 7 days at 245°C, alloy 34.10 was homogeneous, whilst alloys 32.21 and 34.92 contained clear excess of bismuth and of the compound "BiPd" respectively. In chill castings annealed for 7 days at 370°C, alloy 33.41 contained minute traces of chilled liquid whilst alloy 33.40 was homogeneous, and this composition is clearly almost exactly that of the Bi-rich phase boundary. Alloy 35.74 contained a clear excess of the "BiPd" phase.

Taking into account the relative amounts of the phases present, these results suggest that at 370°C the composition of the "Bi_2Pd" phase varies between 33.4 and 34.8% Pd, and that with falling temperature the Bi-rich phase boundary moves slightly in the direction of higher Bi-content.

When an alloy containing 28% Pd was annealed at 400° and quenched, the extracted crystals were no longer needles, but were irregular in shape, with occasional plane faces. This agrees with the conclusion of the thermal analyses (p. 159) that a transformation occurs above the eutectic temperature, in contrast to the Russian equilibrium diagram of Fig. 1 which placed the $\alpha \rightleftarrows \beta$ Bi_2Pd change at 200°C. Careful cooling- and heating-curves were taken of almost pure "Bi_2Pd" and showed no signs of an arrest between 170° and 250°C. Further support for the present diagram was given by the fact that a rotating crystal X-ray diffraction photograph from one of the needle-shaped crystals grown in the present work at 265°C, gave layer lines indicating an interatomic distance (parallel to the needle axis) of 4.30 Å, in agreement with the values 4.26 and 4.28 Å obtained by ZHURAVLEV AND ZHDANOV[1] and by BURR AND PEACOCK[5] for the low temperature modification of "Bi_2Pd".

(e) The BiPd phase

Eight alloys in the equiatomic region were annealed for 11 days at 470°C after a preliminary heat treatment to absorb low-melting constituents. After this treatment, alloy 49.87 was almost homogeneous with minute traces of the Pd-rich phase, whilst alloys 48.62 and 50.56 were clearly two-phase. After annealing for 7 days at 245°C, alloy 50.28 was homogeneous whilst alloys 49.44 and 51* were two-phase. These experiments suggest that the composition of the phase is almost exactly that of the equiatomic ratio, and that any variation in composition is unlikely to exceed 1%.

DISCUSSION

The present equilibrium diagram indicates the same phases as that of the Russian workers, although the temperatures of the liquidus differ widely in places.

Fig. 4 shows the equilibrium diagrams of the systems Pd–Sb and Pd–Bi, and the resemblance is remarkable. In both systems there are compounds of the type Bi_2X and BiX, and the melting points in the antimony alloys are uniformly higher, as would be expected from the more electronegative nature of antimony. Calculation shows that the depression of freezing point of bismuth produced by palladium is that which

* This composition is synthetic. All the remaining values are by chemical analysis.

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would be expected from van't Hoff's equation for monatomic solid and liquid solutions. The compounds Bi_2Pd and BiPd do not therefore appear to exist as compound molecules in the liquid state.

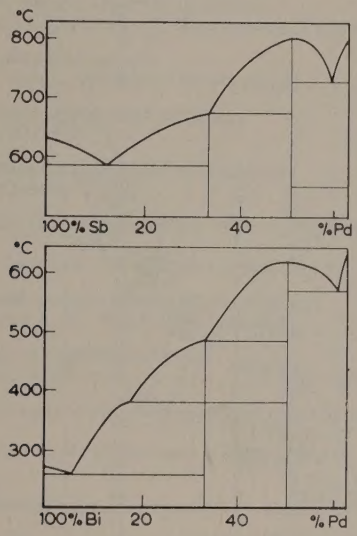

Fig. 4. Sb–Pd and Bi–Pd equilibrium diagrams in atomic percentages.

ACKNOWLEDGEMENTS

The authors must express their gratitude to Professor SIR CYRIL HINSHELWOOD, F.R.S., and Dr. F. M. BREWER for laboratory accommodation and other facilities which have encouraged the present research work. Thanks are also due to Mr. K. G. WOOLMINGTON for assistance with the later annealing experiments. All analyses were carried out by Messrs. Johnson, Matthey & Co., Limited, and thanks are due to Dr. J. C. CHASTON for his care and attention.

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Supplementary Note

Since the above paper was written, an English abstract has appeared of a later Russian paper by N. N. ZHURAVLEV (*Zhur. Eksptl. i Teoret. Fiz.*, 32 (1957) 1305)

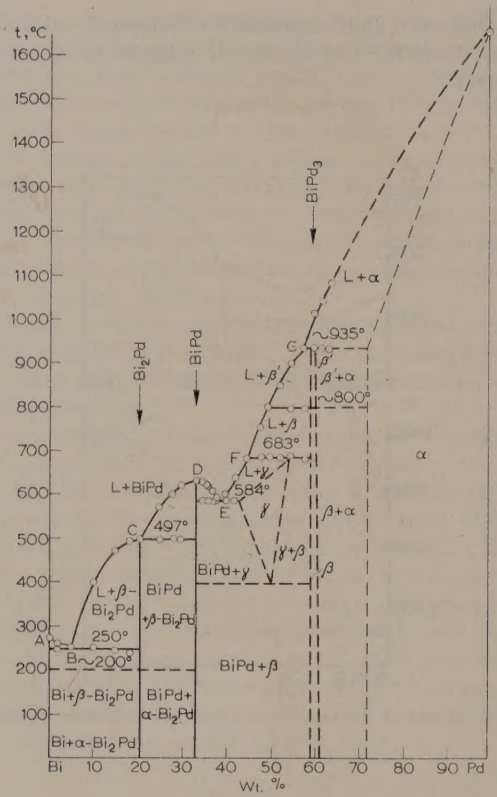

Fig. 5.

whose diagram is shown in Fig. 5. This diagram does not show the transformation at 380 °C established by the present work, whilst there are slight differences between the temperatures of the other horizontals in the diagram and those obtained in the present investigation.

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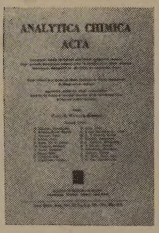

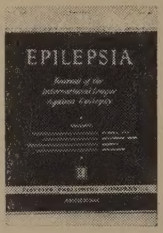

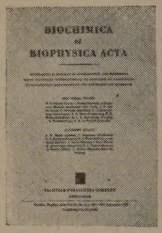

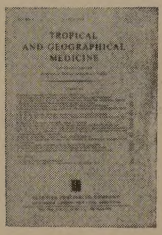

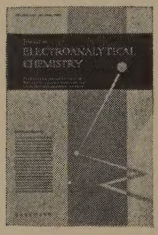

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